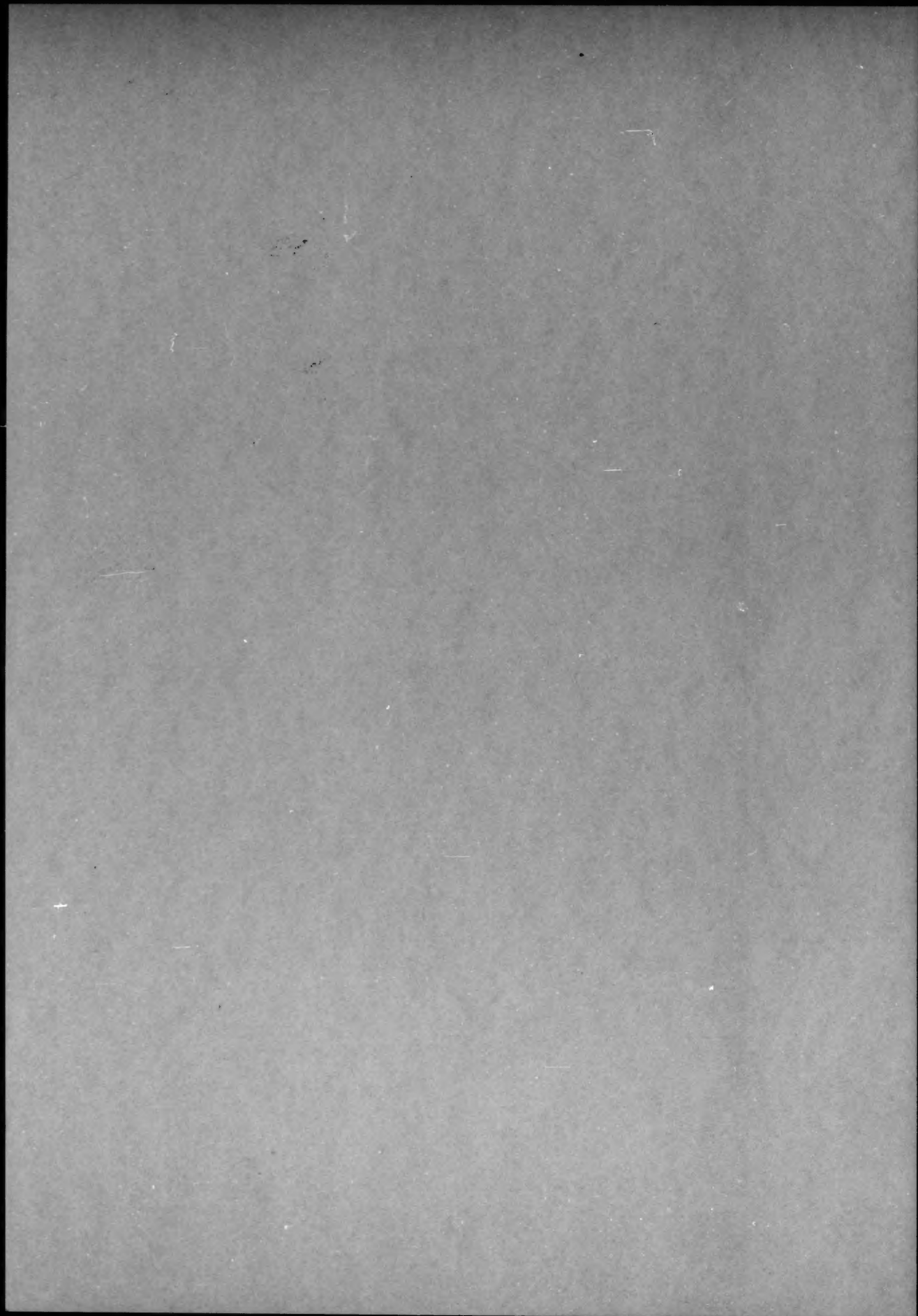


**Journal of General Chemistry**

**Vol. 23 No. 9**



# REACTION OF NITRATES AND NITRITES OF METALS OF THE FIRST AND SECOND GROUPS OF THE D. I. MENDELEEV PERIODIC SYSTEM IN MELTS

## VII. INVESTIGATION OF THE TERNARY SYSTEM LITHIUM, POTASSIUM, AND THALLIUM NITRATES

P. I. Protsenko and I. K. Shelomov

Chemical compounds of monovalent thallium resemble those of the metals of the first group of the D. I. Mendeleev periodic system in all of their physico-chemical properties. But in view of certain individual peculiarities of lithium, which differentiate it from the alkali metals, it seemed important to study the reaction of thallous nitrate with lithium nitrate, and to determine whether or not the above analogy was retained in melts with lithium nitrate.

For the above reason, and also to gather material on the nitrate-nitrite equilibrium of metals of the first and second group of the D. I. Mendeleev periodic system in melts, necessary for the determination of the general laws which govern the course of the reaction, the ternary system, lithium, potassium, and thallous nitrates, was investigated by the thermal method of physico-chemical analysis.

**Binary Systems** Structural diagrams of the system potassium nitrate-thallous nitrate were investigated by A. G. Bergman [1], A. P. Rostkovsky [2], P. K. Leman [3], and others. A repeat investigations by the authors confirmed the general character (Fig. 1). Thallous nitrate does not react chemically with potassium nitrate but forms a simple eutectic containing 28 molecular % of potassium nitrate and 72% of thallous nitrate • melting at 181°.

The diagram of the system lithium nitrate-potassium nitrate was previously studied and reported by one of the authors [4] (Fig. 1). It also shows a complete eutectic containing 58% of potassium nitrate, and 42% of lithium nitrate, melting, at 120°.

The structural diagram of the binary system thallous nitrate-lithium nitrate was newly studied by the authors. The liquidus curve of this system consists of the crystallization of thallous nitrate and crystallization of lithium nitrate branches. The eutectic point corresponds to a composition 70.5% of thallous nitrate and 29.5% of lithium nitrate.

It could be supposed from the character of the binary systems which are the primary constituents of the ternary system potassium-thallous-lithium nitrates, that no chemical reaction between the above components would occur within the ternary system, which was indeed confirmed experimentally.

\* Subsequently the composition is expressed in molecular per cent.

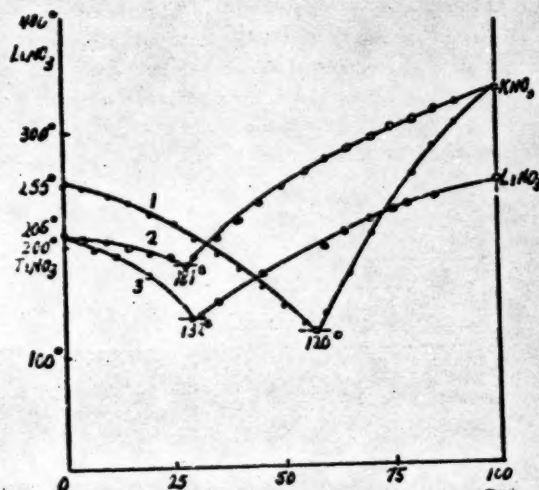


Fig. 1. Binary Systems. 1 -  $\text{LiNO}_3\text{-KNO}_3$ , 2 -  $\text{TlNO}_3\text{-KNO}_3$ , 3 -  $\text{TlNO}_3\text{-LiNO}_3$ .

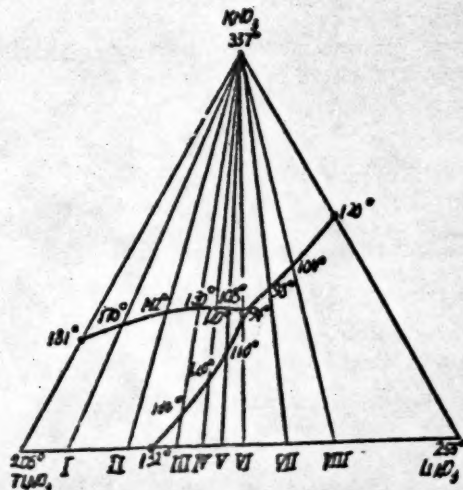


Fig. 2. Direction of sections of the ternary system.



Sections of the Ternary System. In order to study the liquidus surface of the ternary system potassium-thallous-lithium nitrates, 8 sections were investigated, the character and direction of which are shown in Fig. 2. As it is apparent from this figure, all of the sections have the direction from the side thallous nitrate-lithium nitrate to the apex potassium nitrate. Structural diagrams for the sections are given in Figs. 3, 4, and 5.

The crystallization surface was shown (Fig. 6) by means of a projection of the isotherm triangle from the given sections and binary systems. The isotherms were taken through 20°. The composition of the ternary section was found experimentally and was confirmed by an orthogonal projection of the mutual crystallization curves on the side of the triangle, thallous nitrate-lithium nitrate (Fig. 7). The structural diagram of the ternary system thallous, lithium, and potassium nitrates belong to those of the simplest type with a ternary eutectic. The ternary eutectic point corresponds to the composition 34% of potassium nitrate, 33% of lithium nitrate, and 33% of thallous nitrate, and melts at 94°. Lines of mutual crystallization on the liquidus surface of the above system are separated into three crystallization poles: thallous nitrate, the crystallization area of which consists of 22% of the whole triangle, lithium nitrate with a crystallization area of 39%, and potassium nitrate, 39%.

Section No.	Molecular percents			Melting points of the compositions at the transition points
	KNO <sub>3</sub>	LiNO <sub>3</sub>	TlNO <sub>3</sub>	
Ia*	30	7	63	170°
Ib*	33	17	50	142
IIa*	5	34	61	130
IIb*	35	22.5	43.5	130
IIIa*	15	34	51	120
IIIb*	36	26	38	120
IV	25	34	41	110
V	34	30	36	108
VI	34	33	33	94

Notes. a\*—composition at first transition point; b\*—composition at second transition point.

A peculiarity of the given system is the exceptionally low melting point of the ternary eutectic, 94°. The melting point of the ternary eutectic is 112° below that of the lowest melting component of the system, and 26° below that of the lowest melting binary eutectic consisting of lithium and potassium nitrates.

An investigation of the ternary system, thallous, lithium, and potassium nitrates, showed that monovalent thallium nitrate does not display any tendency for chemical reaction with lithium and potassium nitrates, either in binary, or ternary combinations, but forms a simple eutectic mixture with them. Thallous nitrate shows a complete resemblance to the alkali metal nitrates in melts.

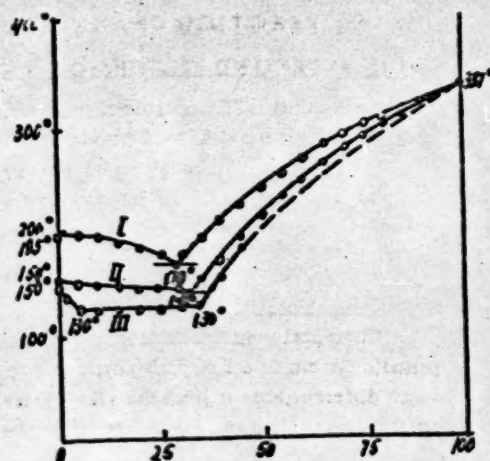


Fig. 3. Sections through the ternary system.

I—90% TlNO<sub>3</sub> + 10% LiNO<sub>3</sub> → KNO<sub>3</sub>  
 II—75% TlNO<sub>3</sub> + 25% LiNO<sub>3</sub> → KNO<sub>3</sub>  
 III—65% TlNO<sub>3</sub> + 35% LiNO<sub>3</sub> → KNO<sub>3</sub>

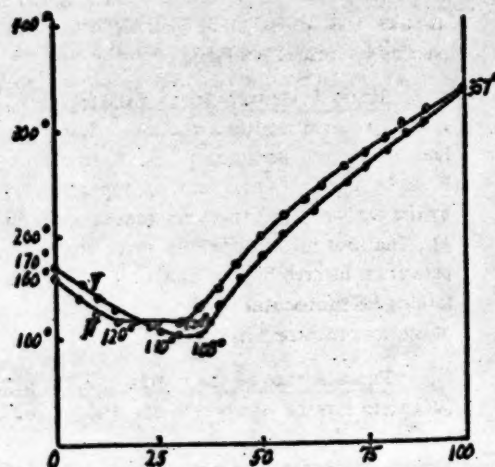


Fig. 4. Section through the ternary system.

IV—60% TlNO<sub>3</sub> + 40% LiNO<sub>3</sub> → KNO<sub>3</sub>  
 V—55% TlNO<sub>3</sub> + 45% LiNO<sub>3</sub> → KNO<sub>3</sub>



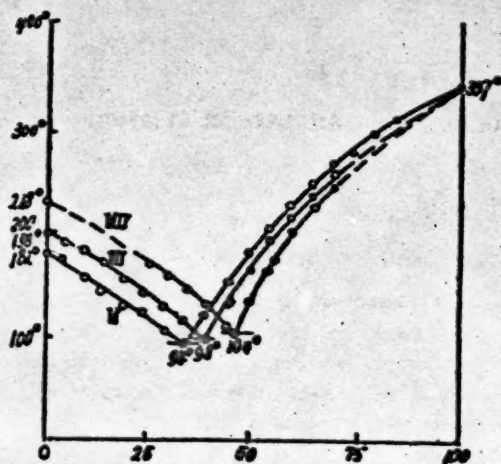


Fig. 5. Sections through the ternary system.  
VI - 50%  $\text{TlNO}_3$  + 50%  $\text{LiNO}_3$  —  $\text{KNO}_3$ ;  
VII - 40%  $\text{TlNO}_3$  + 60%  $\text{LiNO}_3$  —  $\text{KNO}_3$ ;  
VIII - 25%  $\text{TlNO}_3$  + 75%  $\text{LiNO}_3$  —  $\text{KNO}_3$ .

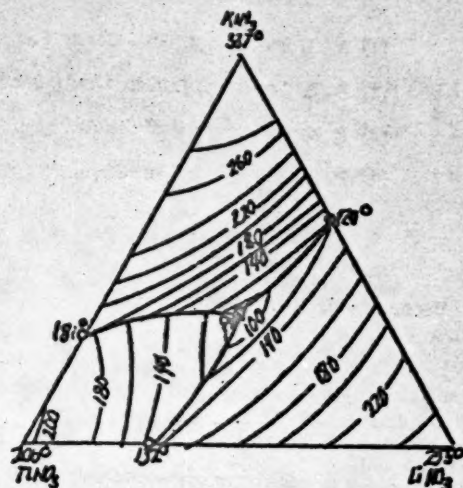


Fig. 6. Projection of the crystallization surface of the ternary system based on a triangle.

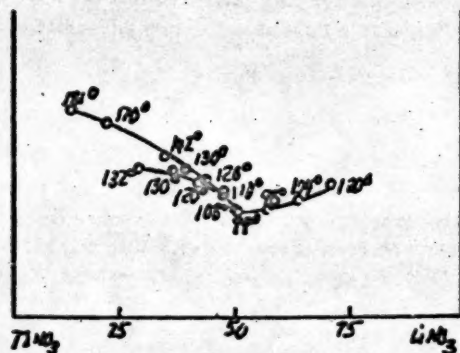


Fig. 7. Projection of the line of mutual crystallization on the side of thallium nitrate - lithium nitrate side.

## SUMMARY

1. The ternary system thallous-lithium-potassium nitrates was investigated by the visual polythermic method of physico-chemical analysis.
2. The binary system thallous nitrate-lithium nitrate studied showed a simple eutectic with the melting point  $132^\circ$  containing 70.5% thallous nitrate and 29.5% lithium nitrate.
3. It was shown that the ternary system belongs to those with one ternary non-variant point of the composition: 34% potassium nitrate, 33% lithium nitrate, and 33% thallous nitrate, and melting point  $94^\circ$ .
4. It was shown that thallous nitrate, because of its great resemblance in all of its physico-chemical properties to lithium and potassium nitrates, does not participate in chemical reaction in melts, but forms eutectic mixtures with them in binary, as well as ternary systems.

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Received March 17, 1953

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\* See Consultants Bureau English translation, page 1357.

## PREPARATION OF PHOSPHOTUNGSTIC ACID FROM PHOSPHORIC AND TUNGSTIC ACIDS

E. A. Nikitina, O. N. Sokolova, and I. I. Angelov

An analysis and experimental evaluation of literature results on the methods for the preparation of phosphotungstic acid has been given in a paper by one of the authors [1]: the best results of all the methods tested, in relation to obtaining an individual preparation, were given by the ether procedure with two subsequent treatments of the heteropoly acid with ether. In spite of the fact that the above method makes it possible to obtain the individual substance, it still contains inconveniences which are inevitable when one works with such volatile solvents as ether. For this reason, a method for the synthesis of phosphotungstic acid was subsequently developed which circumvented the stage of the formation of its etherate. Rosenheim [2] considers that "the direct synthesis of heteropolyacids is only possible in exceptional cases, as for example, with luteo compounds and only with poor yields."

An attempt for the direct synthesis of phosphotungstic acid from tungstic anhydride and phosphoric acid in aqueous solution is reported in Hastings and Frediani's paper [3]. In spite of the fact that the authors employed a twofold excess of phosphoric acid in one of the experiments, phosphotungstic acid was not obtained.

It is believed that the lack of success was due to the fact that they used tungstic anhydride for the synthesis, which is a substance with insufficient reactivity.

The authors decided to employ tungstic acid for the synthesis. For this reason it was necessary, first of all, to determine whether the reaction between tungstic and phosphoric acid proceeds according to the equation:



Freshly precipitated tungstic acid and phosphoric acid (d 1.511) were used as the starting materials.

Tungstic acid was prepared from sodium tungstate dissolved in water, calculated for a ratio of 1:6 relative to the weight of the salt used. The solution was filtered, and the tungstic acid was precipitated from it by the addition of a thin stream of concentrated nitric acid with continuous stirring until complete precipitation. The white curdy precipitate of tungstic acid obtained was filtered on a porcelain filter and washed with distilled water until the absence of a reaction for  $\text{NO}_3^-$  in the residue (test with diphenylamine and sulfuric acid). The residue was then sucked and analysed for the amount of  $\text{H}_2\text{O}$  in it. The tungstic acid obtained by this method contained about 20% of  $\text{WO}_3$ .

The tungstic acid, analyzed for water content, was used for the preparation of phosphotungstic acid.

A weighed sample of about 100 g of tungstic acid of known  $\text{WO}_3$  content was placed into a 1 liter round bottom flask. Phosphoric acid, in an amount greater than calculated by the above equation, was added to it.

The total volume of the reaction mixture was brought to about 0.5 liters by the addition of water; the reaction mixture obtained in this manner was boiled for several hours with continuous mechanical stirring, keeping the volume constant. The reaction mixture was then cooled, filtered from the unreacted tungstic acid, and the filtrate evaporated in order to isolate the crystals of phosphotungstic acid.

In the first two experiments, the tungstic acid obtained from 200 g of sodium tungstate was washed with water heated almost to boiling, wherein the filtration of the residue on the funnel was alternated with stirring in a beaker with hot water. The initially white, curdy residue became at the end of the washing bright yellow and assumed the form of separate hard granules. Two experiments on the synthesis of phosphotungstic acid were conducted with this yellow preparation. Heating of the reaction mixture lasted for 6 hours in one case, and 15 in the other. But in both cases, the complex formation reaction occurred only to an insignificant degree; much unused tungstic acid remained which passed through the filter during filtration (colloidal tungstic acid). In the second experiment, 15 ml of concentrated hydrochloric acid was added to the reaction mixture before filtration. The solution was boiled, and the residue of the tungstic acid was then completely filtered. The transparent filtrate was evaporated on the water bath until complete removal of the hydrochloric acid, and then to dryness, but no crystals of phosphotungstic acid could be obtained. Only a thin crystalline film of non-volatile substances was formed on the bottom of the dish, which was washed out from the reagents used.



The yellow monohydrate of tungstic acid was, therefore, practically incapable of participating in a complex formation reaction with phosphoric acid.

A series of orientating experiments was then conducted on the washing of the tungstic acid with water heated to various temperatures in order to determine under what conditions a more reactive tungstic acid would be obtained.

Tungstic acid was precipitated from 200 g of sodium tungstate, filtered on a porcelain filter, and separated into four parts. Each of these was washed until the absence of a reaction for  $\text{NO}_3^-$  in the residue, with water heated to various temperatures.

250 ml of water was used for each wash. The temperature of the water, the amount of washings, and the external appearance of the washed tungstic acid is given in Table 1.

TABLE 1

Results of the Washing of Tungstic Acid

Expt. No.	Temperature (in °)	Number of washings	External appearance of the washed acid
1	80	4	Yellow having the form of granules.
2	70	5	Light yellow, almost completely curdy
3	60	6	Light yellow, curdy
4	50	6	" " "

At the end of the washing, all four of the residues were placed into flasks, and 2 ml of phosphoric acid and 150 ml of water added to them; the solutions obtained were boiled for 2 hours, cooled to room temperature, and the volume of all of the solutions adjusted to 100 ml.

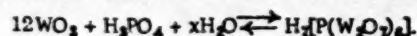
In order to determine in what case the complex formation reaction proceeded the most completely, the following method was used: 15 ml of the solution was removed from each flask and 5 ml of quinoline acetate added to each. By the size of the precipitate formed, it could be judged in which solution more of the complex anion could be found. The amount of precipitate was approximately equal for the last three samples, and considerably less in the first.

In subsequent experiments the washing of the tungstic acid was effected with water heated to 60-70°.

Later, a series of experiments was conducted in order to determine how much the reactivity of the tungstic acid changes with time (aging).

Tungstic acid was prepared from 500 g of sodium tungstate, washed, and analyzed for the amount of water in it.

Part of the tungstic acid was used for the preparation of phosphotungstic acid directly after the washing, the second experiment with the same tungstic acid was conducted after one day, the third, after two days, and the fourth three days after the washing of the starting preparation. Before each experiment, the tungstic acid was carefully mixed and analyzed for the amount of  $\text{H}_2\text{O}$ . The phosphoric acid was added in an amount based on the amount of  $\text{WO}_3$  used, according to the equation:



The volume of the reaction mixture in all experiments was adjusted to 0.5 liters by the addition of water; the boiling with continuous stirring and constant volume (periodic addition of water) lasted for 6 hours.

In all experiments, part of the tungstic acid did not react; very little of it remained in the first experiment, in comparison to the others. The amount of  $\text{H}_2\text{WO}_4$  noticeably increased from the first to the fourth experiment.

The residue was filtered through a double thickness filter (the filtrates all were cloudy), and was analyzed for the amount of water in it after weighing.

The amount of starting tungstic acid remaining in the residue, as well as the per cent  $\text{WO}_3$  used, is given in Table 2.

From the data in Table 2, it is apparent that the reactivity of tungstic acid is greatly diminished with aging. It is necessary to use tungstic acid for complex formation directly after the washing.

As it was stated above, the solution at the end of the synthesis, filtered poorly because the remaining tungstic acid passed through the filter. A series of experiments was conducted to determine conditions under which the precipitate could be separated completely.

The filtrates obtained in experiments 2, 3, and 4 (Table 2) were combined, mixed well, and filtered under various conditions; namely, through one- and two-sheet paper filters on a porcelain filter, and through the same amount of filters on the usual funnel; the filtrate was always cloudy but somewhat clearer in the last case. The

TABLE 2

Effect of Aging of Tungstic Acid on the Process of Complex Formation

Expt. No.	Time between the preparation of $H_2WO_4$ and its use for the complex formation reaction	Used for the synthesis (in g)		Remaining (in g)		Percent $WO_3$ used
		Moist $H_2WO_4$	Amount of $WO_3$	Moist $H_2WO_4$	Amount of $WO_3$	
1	Directly after washing	115	20.9	6	1.67	92.0
2	18 hours	108	20.4	42	7.0	65.7
3	2 days	117	23.0	68	13.5	41.3
4	3 days	111	22.3	83	16.0	28.2

filtration without vacuum proceeded slowly; then a paper filter was placed on a porcelain funnel and a thin dense layer of washed tungstic acid placed upon it, which served as a filter. The residue was retained completely in this case.

As it was established, the reaction between tungstic and phosphoric acids does not go to completion. For this reason the filtrate, in addition to the phosphotungstic acid, contains some free phosphoric acid. In order to obtain pure preparations, a crystallization has to be effected in the presence of the mother liquor which is difficult because the acid is very soluble in water and crystallizes with a large number of molecules of water.

Experiments conducted showed that it was best to evaporate the filtrate until the appearance of the first crystals on the surface of the solution or on the bottom of the dish; then the solution must be cooled to room temperature, and the deposited crystals of phosphotungstic acid must be separated at once. If the above is not done, an almost continuous mass of fine crystals is formed which is difficult to separate from the mother liquor.

From the filtrate obtained in experiment 1, Table 2, 14.5 g of crystals was isolated which were then recrystallized; 8.1 g of phosphotungstic acid was obtained. The  $P_2O_5$  content in it amounted to 2.47%, based on the anhydrous preparation (theoretical yield 2.49%).

Therefore, pure phosphotungstic acid can be obtained by means of the above method.

Therefore, conditions were found as a result of the experiments conducted, under which the reaction between tungstic and phosphoric acids proceeded to a sufficient degree of completion, and a method for the preparation of phosphotungstic acid without the use of ether was developed.

The recommended method consists of the following: tungstic acid is precipitated from a solution of sodium tungstate with the aid of nitric acid, which is filtered and washed with distilled water heated to 60–70° until a negative reaction for  $NO_3^-$  in the residue. The acid obtained is analyzed for the amount of water in it, and is used at once for the preparation of phosphotungstic acid. The synthesis is conducted as reported above. At the end of the synthesis, in order to hasten the filtration, the solution is evaporated to  $\frac{3}{4}$  of the volume and filtered while hot through a thin layer of washed tungstic acid. The transparent filtrate is evaporated until the appearance of the first crystals, and the isolation of these is effected as stated above.

Two samples of phosphotungstic acid were prepared by means of the proposed method.

The amount of tungstic acid used, the yield, and the results of analysis of the samples obtained are given in Table 3.

TABLE 3.

Results of Experiments on the Preparation of Phosphotungstic Acid

Sample No.	Used (in g)		Remaining (in g)		% $WO_3$ used	Heteropolyacid obtained (in g)		% Yield based on $WO_3$ reacted	$P_2O_5$ in the phosphotungstic acid (in %)	Amount of mother liquor (in ml)
	Moist $H_2WO_4$	$WO_3$	Moist $H_2WO_4$	$WO_3$		Hydrate	Anhydrous			
1	360	79.2	32	7.2	91	27.4	23.6	32.7	2.46	1–12 2–5
2	540	91.8	68	12.0	87	32.8	27.2	34.1	2.52	1–17 2–6

The yield of the heteropolyacid is given in relation to the tungstic acid reacted.

It is better to evaporate the mother liquors separately. The amount of phosphoric acid remaining in the mother liquor increases with the separation of the crystals of phosphotungstic acid; they must be combined with the initial solution for the synthesis of phosphotungstic acid.

The remaining tungstic acid was placed into a flask and  $H_3PO_4$  was added to it in a quantity greater than necessary, by calculation, for the preparation of the heteropoly acid, and the mixture boiled for two hours; about 2% of the tungstic acid used reacted. Therefore, the remaining tungstic acid is not very reactive and cannot be used directly for the synthesis of phosphotungstic acid; it must be reconverted with sodium hydroxide into sodium tungstate and the solution obtained combined with the sodium tungstate solution for the separation of tungstic acid from it for a new synthesis of the compounds.

$P_2O_5$  was determined in the form of magnesium pyrophosphate; the precipitation of the ammonium magnesium phosphate salt was effected during the cooling of the solution to 3-5°; the tungsten was precipitated with quinoline after the removal of the  $P_2O_5$ .

For the determination of  $Na_2O$ , the heteropolyanion was precipitated with quinoline acetate, and the sodium determined as  $Na_2SO_4$ ; the water determined by heating a sample to constant weight.

#### SUMMARY

1. Conditions were found for the preparation and washing of tungstic acid capable of a complex formation reaction with phosphotungstic acid; it was shown that the ability of tungstic acid for complex formation changes with time.
2. A new method for the direct synthesis of phosphotungstic acid from phosphoric and tungstic acids without the use of ether was developed.
3. Methods are given for the use of waste products: unreacted tungstic acid and the mother liquors containing excess phosphoric acid.
4. The yield of the preparation was about 33% based on the tungstic acid reacted.

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Received October 7, 1952

Institute of Chemical Reagents



## INVESTIGATIONS OF POLYTHIONIC ACIDS

### II. HYDROLYSIS OF SULFUR DICHLORIDE

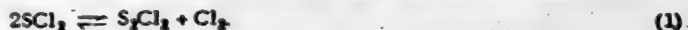
I. V. Yanitsky and E. I. Patsauskas

Almost all of the investigators working recently on the chemistry of polythionic acids agree that these acids are formed by means of some unstable intermediate substance from other sulfur compounds. Among these unstable intermediate substances, the hypothetical hydrosulfurous acid must be of great importance, as was shown, even in 1935, by one of the authors [1]. This suggestion was confirmed experimentally by Goehring by the hydrolysis of esters and alkyl amides of hydrosulfurous acid [2]. Goehring found pentathionic acid among the products of the hydrolysis of diethyl hydrosulfite; the semi-quantitative character of her experiments, however, does not allow a conclusion to be made on the mechanism of the formation of the final products of the spontaneous decomposition of hydrosulfurous acid.

Sulfur dichloride can be considered a derivative of hydrosulfurous acid; i.e., its acid chloride. For this reason it could be expected that the primary products of the reaction of sulfur dichloride with water would be hydrogen chloride and the unstable hydrosulfurous acid, and that an analytical study of the isolated products of the hydrolysis of sulfur dichloride under various conditions would throw light on the reactions of hydrosulfurous acid, and in particular, those leading to the formation of polythionic acid.

The aim of the present investigation was the systematic study of the hydrolysis of sulfur dichloride, mainly on the relation of the hydrolysis products to the acidity of the medium, which is very important as is known [1] for the formation of polythionic acids.

Experimental method. Specially prepared sulfur dichloride containing 32.0% S and 68.0% Cl was used as the starting material. Certain deviations from the stoichiometric composition of  $\text{SCl}_2$  (31.1% S and 68.9% Cl) were predicted by the fact that sulfur dichloride, although slowly, dissociates partly according to the equation [3]:



For this reason, a small excess of sulfur over the stoichiometric composition, in other words, a small impurity of  $\text{S}_2\text{Cl}_2$  was necessary to avoid a considerable shift of this equilibrium to the right. The sulfur dichloride prepared was stored at 0° in sealed ampoules.

Experiments on the hydrolysis were conducted in the following manner: A sealed ampoule, with an accurately known amount of sulfur dichloride, was placed into a thick-walled bottle and covered with water, or the solution of the desired composition. The ampoule was broken by energetic shaking of the hermetically sealed bottle, which signified the start of the reaction. The end of the hydrolysis was readily established visually as the liquid sulfur dichloride is not miscible with water. A considerable amount of colloidal sulfur separates during the course of the reaction. After its coagulation by means of lanthanum or aluminum chloride, the reaction mixture was filtered through a tared filter; the filtered and washed sulfur was dried at room temperature in a desiccator and weighed. The mother liquor was subjected to quantitative analysis [4].

Hydrolysis of sulfur dichloride in pure water. The results of four experiments are given in Table 1, in which 5–10 g of  $\text{SCl}_2$  was hydrolyzed in 400–500 ml of pure water. The analysis of the reaction mixture was effected in separate experiments after several intermediate times (4–19 hours) from the start of the reaction. The results are more conveniently expressed as the per cent sulfur found in the form of the isolated reaction products in a ratio to the total starting amount.

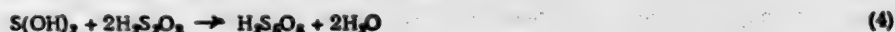
The experiments of this series show that the predominant reaction products are pentathionic acid and elementary sulfur. The relative amount of pentathionic acid decreases with time, and that of sulfur increases. This undoubtedly results from the slow decomposition of pentathionic acid [5]. Tetra and trithionic acids must also be considered as products of the decomposition of pentathionic acid, small quantities of which were found in experiment 4; i.e., 19 hours from the start of the hydrolysis of sulfur dichloride. The absence of both these acids in the first three experiments leaves no doubt that the first of the polythionic acids was pentathionic acid.

It is also important that in all experiments thiosulfuric acid was found, although in small amounts. This enables the mechanism of the basic reaction, the formation of pentathionic acid, to be expressed by the equations

TABLE 1

## Hydrolysis of Sulfur Dichloride in Pure Water

Expt. No.	1		2		3		4	
SCl <sub>2</sub> used (in g)	4.369		9.640		7.365		8.142	
Hydrolysis time* (in hrs)	4		12		15		19	
Reaction products	Milli-moles	% S	Milli-moles	% S	Milli-moles	% S	Milli-moles	% S
H <sub>2</sub> SO <sub>3</sub>	0.41	0.9	0.63	0.7	0.32	0.4	2.98	3.7
H <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	0.585	2.7	0.48	1.0	0.32	0.9	0.165	0.4
H <sub>2</sub> S <sub>3</sub> O <sub>3</sub>	0	0	0	0	0	0	1.94	7.1
H <sub>2</sub> S <sub>4</sub> O <sub>3</sub>	0	0	0	0	0	0	0.52	2.6
H <sub>2</sub> S <sub>5</sub> O <sub>3</sub>	6.826	77.9	13.66	70.1	9.51	64.6	6.87	42.2
H <sub>2</sub> SO <sub>4</sub>	3.02	6.9	3.23	3.3	4.33	5.9	7.90	9.7
S	5.66**	13.0	23.28**	24.2	20.81**	28.2	29.43**	36.1



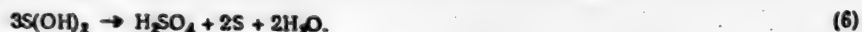
The amount of elementary sulfur formed in all experiments, however, was too great to be explained by the decomposition of pentathionic acid. The usual decomposition of thiosulfuric acid



cannot be of much significance here, since in all cases the reaction mixture contained only very small amounts of sulfur dioxide. In addition, the latter can also be the product of the decomposition of polythionic acids. Therefore, elementary sulfur must be a waste product of a side reaction occurring parallelly with the formation of pentathionic acid.

The constant presence of considerable amounts of sulfuric acid in the reaction mixture had to be kept in mind. Sulfuric acid cannot be a decomposition product of polythionic acids in the given case, since significant amounts of sulfate ions are formed by the decomposition of trithionic acid [5], which was not found in any quantity in the first three experiments. Therefore, sulfuric acid also is a product of a side process which accompanies the formation of pentathionic acid.

A study of the reaction of esters of hydrosulfurous acid with various reducing agents [2] showed that hydrosulfurous acid possesses strong oxidizing properties in addition to its long-known reducing properties; the product of its reduction usually is elementary sulfur. The above resulted in speculation that the formation of sulfuric acid, also partially the formation of elementary sulfur in these experiments is the result of one and the same process, the auto oxidation of hydrosulfurous acid



In experiments 2-4, the amount of sulfur formed was considerably greater than the ratio  $\text{S}:\text{H}_2\text{SO}_4 = 2:1$ , necessary from this equation. But in experiment 1, in which the analysis of the reaction mixture was conducted a short time after the start of the hydrolysis, this ratio was equal to 1.87:1; i.e., approximately equal to that required by equation (6). In the rest of the experiments of this series, the amount of elementary sulfur increased, evidently, as a result of the slow decomposition of pentathionic acid.

It must also be mentioned that the relative amounts of sulfuric acid found in all of these experiments were of the same order, and even less than found by Goehring [2] during the hydrolysis of ethyl hydrosulfite. Therefore, it must be deemed unnecessary to consider the oxidation of sulfur compounds by chlorine as a possible explanation for the formation of sulfuric acid; i.e., a noticeable dissociation of sulfur dichloride according to equation (1).

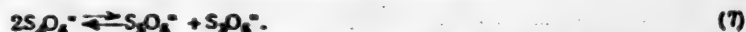
\* Time from the start of the experiment to the moment of analysis.

\*\* Amount of S in Tablets 1, 2, 3 and 4 is in milli-atoms.

Hydrolysis in acetate buffer. Because hydrochloric acid is formed during the hydrolysis of sulfur dichloride in pure water, the reaction of hydrosulfurous acid leading to the formation of the end products which were detected by analysis, proceeds in strong acidic medium. For this reason, in order to study these reactions in weakly acidic media, sulfur dichloride was hydrolyzed in the subsequent experiments in acetate buffer solution containing a large excess of the buffer substance. The results of one experiment at pH 4.7 (Table 2) are given as an example. From the data of Table 2, it is apparent that a large amount of sulfur dichloride is

transformed into polythionic acids; however, in addition to pentathionate, much trithionate and tetrathionate was found. These appear evidently as a result of the large value of the pH relative to that of previous experiments, because the stability of pentathionic acid decreases with the decrease in acidity of the medium, and it decomposes with the formation of the lower polythionate [5].

A more important difference in comparison with the results of hydrolysis in pure water is the presence of very considerable amounts of thiosulfate here. Thiosulfate becomes stable [6] at  $\text{pH} > 4$ ; for this reason there appear to be conditions for the shift of the equilibrium of equation (3) to the right and for the decrease in the rate of formation of pentathionate according to equation (4) [1, 7]. Pentathionate, at the low acidity of the medium, readily cleaves 1 atom of sulfur [5], and the tetrathionate formed in this manner is itself decomposed according to the equation



The latter reaction is extremely accelerated catalytically by thiosulfate [8]. Therefore, it becomes understandable why the lower polythionates appeared in considerable amounts in these experiments even an hour after the start of the hydrolysis of sulfur dichloride.

Hydrolysis in hydrochloric acid. In the experiments described above on the hydrolysis of sulfur dichloride in pure water, all of the reactions proceeded with the exception of the first moment of the hydrolysis, in acidic media but under conditions of a gradual increase in the concentration of hydrogen ions since the products of these reactions are strong acid - hydrochloric and pentathionic acid. In order to verify whether a large change in the concentration of free acid had a noticeable effect on the results of the reaction, sulfur dichloride was hydrolyzed, in subsequent experiments, in a large excess of 2 N hydrochloric acid (400-500 ml). Under these conditions the change of concentration of hydrogen ions during the reaction can be considered almost insignificant. Data of three experiments are given, in which the analysis of the reaction mixture was conducted at various periods of time after the start of hydrolysis (Table 3).

TABLE 3

Hydrolysis of Sulfur Dichloride in 2 N Hydrochloric Acid

Expt. No.	6		7		8	
Used:						
$\text{SCl}_2$ (in g)	5.338		6.287		6.810	
Hydrolysis time (in hrs)	2.5		3.5		12	
Reaction products	Milli-moles	% S	Milli-moles	% S	Milli-moles	% S
$\text{H}_2\text{SO}_3$	0	0	0.08	0.1	0.93	1.3
$\text{H}_2\text{S}_2\text{O}_3$	4.15	15.5	2.77	8.8	1.99	5.8
$\text{H}_2\text{S}_4\text{O}_6$	7.08	56.3	7.53	59.9	9.02	66.4
$\text{H}_2\text{S}$	Traces	0.0	0.63	1.0	0	0
$\text{H}_2\text{SO}_4$	5.30	9.9	7.17	11.4	2.37	3.5
S	6.46	12.1	10.97	17.3	15.72	23.0



The general picture here is almost the same as for the hydrolysis in pure water. Characteristically, here the main product is pentathionic acid; the lower polythionic acids are not found at all. The only essential difference, in comparison to hydrolysis in pure water, was the presence of considerable amounts of thiosulfuric acid. This must be explained by the fact that the stability of the latter, at large concentrations of the side acids, increases with increase of the concentration of hydrogen ions [9].

**Hydrolysis in alkaline medium.** Polythionates do not usually form in alkaline medium. But the hydrolysis of sulfur dichloride in alkaline solution was of interest because of the fact that here the formation of large amounts of thiosulfate could be expected. This view results from the following considerations. According to the above hypothesis, pentathionate is formed in acidic medium not directly from hydrosulfurous acid, but through thiosulfuric acid. Therefore, reaction (3) must be of great importance during the hydrolysis of sulfur dichloride. Hydrosulfurous acid is considered weak, while thiosulfuric acid is a strong acid; for this reason equilibrium (3) is shifted to the right with decrease of the concentration of the hydrogen ions. That the above is actually true is already shown by the results of the hydrolysis of sulfur dichloride in acetate buffer, where a considerable amount of thiosulfate is formed. If the above assumptions were correct, hydrolysis in alkaline medium should lead to the formation of still more thiosulfate. This was verified completely by experimental results: in experiment 9 (Table 4) about 60% of sulfur taken in the form of  $\text{SCl}_2$  was transformed into thiosulfate.

TABLE 4

Expt. No. 9. — Hydrolysis of 2.576 g  $\text{SCl}_2$   
in 150 ml 0.8 N NaOH

Hydrolysis time	1.5 hrs		10 days	
	Milli- moles	% S	Milli- moles	% S
$\text{SO}_3^{2-}$	0.74	2.9	2.35	9.1
$\text{S}_2\text{O}_3^{2-}$	7.38	57.2	7.68	59.6
$\text{S}_2\text{O}_8^{2-}$	0.60	7.0	0	0
$\text{SO}_4^{2-}$	1.87	7.3	2.12	8.2
S	5.56	21.6	5.56	21.6

thionate disappears with time, decomposing, as usual in alkaline medium, into thiosulfate and sulfite according to the equation:



For the formation of trithionate by any method known up to now, the presence of ions of sulfuric acid is necessary [1,2]. In the above case, a more probable path for the formation of trithionate is the reaction of hydrosulfurous acid with bisulfite ions:



But here a question arises in what manner is the sulfate formed during the hydrolysis, which upon first analysis is found in very small amounts. It can be supposed that the autoxidation reaction of hydrosulfurous acid (equation (6)) proceeds in two steps, of which the first leads to the formation of sulfurous acid:



It is also possible that the last reaction is an independent side process which occurs simultaneously with the other transformations of hydrosulfurous acid under the given conditions of acidity.

The reaction leading to the formation of trithionate must, however, be evaluated as a side process during the hydrolysis of sulfur dichloride in alkaline medium, since the main product of the reaction is thiosulfate, formed as a result of the shift of equilibrium (3) to the right.

The following simple calculation may be given in favor of the authors' treatment of the hydrolysis of sulfur dichloride in alkaline medium. Elementary sulfur is formed as a result of the side reactions (8) and (9); namely, 2 g-atoms for 1 mole of sulfate formed, and 1 g-atom for 1 mole of sulfite. According to equation (8), 2 moles of sulfite are consumed for the formation of trithionate. Therefore, if the sulfite were formed according to equation (9) and were partially consumed for the formation of trithionate, then as many gram-atoms of sulfur must have separated as the moles of sulfite found plus double the number of moles of trithionate formed plus double the

However, somewhat unexpected was the presence of a small amount of trithionate, because polythionates, as stated above, do not usually form in alkaline media. The formation of trithionate can be explained by the heterogeneous primary hydrolysis reaction of sulfur dichloride, since the latter is practically immiscible with water and aqueous solutions. A momentary appearance of a certain excess of hydrogen ions is possible as a result of reaction (2) in the boundary layer between the two liquid phases; i.e., conditions in which the formation of polythionates may occur. Since trithionate is the only polythionate which is capable of existing for any length of time in alkaline medium, its presence can be detected soon after the completion of the hydrolysis of sulfur dichloride. From the results it is also apparent that tri-

number of moles of sulfate found. According to the data of Table 4, the amount of elementary sulfur calculated in this manner is equal to:

$$0.74 + 2 \cdot 0.60 + 2 \cdot 1.87 = 5.68 \text{ milli-atoms,}$$

while 5.56 milli-atoms of sulfur were found; i.e., an amount very close to the calculated.

In conclusion it must be mentioned that these experimental results on the hydrolysis of sulfur dichloride in alkali medium differ widely from the data of Goehring on the alkaline hydrolysis of ethyl hydrosulfite [2]. Goehring found approximately the same amount of thiosulfate and sulfite, and traces of sulfide, but no sulfur at all. Her results, however, arouse doubts, since they give no satisfactory sulfur balance. In addition, if there are considerable amounts of oxidation products of hydrosulfurous acid (for example, sulfite) among the reaction products, then they must be accompanied by equivalent amounts of reduction products, which Goehring, besides traces of sulfide, did not find. For this reason her conclusion that sulfite was a main product, in addition to thiosulfate, of the spontaneous decomposition of hydrosulfurous acid in alkaline medium cannot be considered proved.

#### SUMMARY

1. The unstable hydrosulfurous acid formed during the hydrolysis of sulfur dichloride, is transformed into a mixture of products, the nature of which and relative amounts of which depend on the acidity of the medium.
2. By the hydrolysis of sulfur dichloride in pure water; i.e., under conditions of acidity which arise from the products of hydrolysis themselves, the main process is the transformation of hydrosulfurous acid into pentathionic acid.
3. Hydrolysis of sulfur dichloride in solutions of hydrochloric acid leads mainly to the same processes and products as hydrolysis in pure water.
4. Decrease of the concentration of hydrogen ions and its stabilization by acetate buffer lead to a partial stabilization of the thiosulfate formed; increase of the pH favors the secondary reactions leading to the formation of tetra- and trithionate.
5. In alkaline media the main reaction of hydrosulfurous acid is its transformation into thiosulfate.
6. A side reaction proceeds in all cases, in addition to the main one of hydrosulfurous acid given above, as a result of which elementary sulfur and sulfuric acid, or correspondingly, sulfate, are formed. This side reaction is evidently the auto-oxidation of hydrosulfurous acid.

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Received April 6, 1953

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# INVESTIGATION OF POLYTHIONIC ACIDS

## III. FORMATION OF POLYTHIONIC ACIDS

### FROM SULFUR DICHLORIDE AND THIOSULFATE

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Even in 1870 D. I. Mendeleev believed that the structural formulas proposed by him for the polythionic acids could serve as starting points for the development of satisfactory methods for the preparation of these acids or their salts [1]. This soon stimulated the Belgian chemist, Spring, to attempt to synthesize trithionate and pentathionate by the action of sulfites and thiosulfates on sulfur dichloride. Spring actually obtained trithionate by shaking sulfur dichloride with a solution of potassium sulfite, but his attempts to obtain pentathionate by an analogous method; i.e., by using thiosulfate instead of sulfite, were unsuccessful [2].

The synthesis of pentathionate from sulfur dichloride and thiosulfate was only recently accomplished by Goehring and Feldman [3]. It is based on the reactions:



The above authors, however, could not avoid side reactions during this synthesis, which proceeded to a considerable extent, as a result of which, under the conditions recommended by them, some elementary sulfur was formed. This is understandable since the formation of pentathionic acid, according to equation (2) requires a considerably acidic medium; i.e., not less than that in which the acid anions of the strong thiosulfuric acid [4] can be formed. The latter, as is known, is unstable and decomposes into sulfurous acid and sulfur, which leads, without taking into account the extreme instability of hydrosulfurous acid, to a series of side processes, and finally, to the side products of the synthesis.

In order to realize reaction (2) in such a way that it is least accompanied by side processes, it is necessary to introduce the hydrosulfurous acid at the moment of its formation; i.e., to hydrolyze sulfur dichloride in a solution of thiosulfuric acid in which the latter does not cleave sulfur. Two possibilities exist. The first is the use of thiosulfate in weakly acidic medium, as it cleaves sulfur only very slowly at  $\text{pH} > 3$ ; the second is the use of freshly prepared Gil-Beato's solution containing essentially free thiosulfuric acid [5] as the medium for the hydrolysis of sulfur dichloride.

Both methods were tried with the first not leading to the desired results. For this reason, without going into detail, it can only be mentioned that the formation of pentathionate occurs according to equation (2) in weakly acidic medium ( $\text{pH}$  3 to 5), although it is masked to a great extent by side processes. In addition to pentathionate, considerable amounts of tetrathionate and elementary sulfur, as well as small amounts of trithionate and sulfate, are formed. Evidently, the rate of reaction (2) is too slow under these conditions since the concentration of acidic thiosulfuric anions, or the free acid, does not acquire a noticeable value under the given acidity of the medium. Because of this fact, the primary hydrolysis product of sulfur dichloride, hydrosulfurous acid, is not able to react quantitatively with thiosulfate, and partially decomposes in different directions, apparently, as it does in the absence of thiosulfate [6].

Because reaction (2) is related to the consumption of hydrogen ions, a considerable increase in its rate could be expected by the use of thiosulfuric acid in a sufficiently acidic medium, which is Gil-Beato's solution. This view, as will be shown below, was completely proved. In addition, the study of the action of this solution on sulfur dichloride led to a new method for the preparation of solutions of polythionic acids; i.e., six and more atoms of sulfur in the molecule.

#### EXPERIMENTAL

150 ml of concentrated hydrochloric acid ( $d$  1.175) was cooled to  $-20^\circ$ ; a weighed amount of thiosulfate, initially dissolved in a small amount of water, was added with gentle shaking to the cold acid. Only sodium chloride precipitated. An ampoule containing an accurately weighed amount of sulfur dichloride was introduced into the Gil-Beato solution obtained in this manner, the bottle was tightly stoppered, and the ampoule was broken by shaking. At the end of the hydrolysis (disappearance of  $\text{SCl}_2$ ), the solution obtained was transferred into a volumetric

flask and diluted to 200 ml with concentrated hydrochloric acid. The solution was stored at 0°. The analysis was conducted by a method, developed by one of the authors, for Gil-Beato's solution, and which made possible the determination of thiosulfuric acid, the number of moles of polythionic acid, average number of sulfur molecules in the latter ( $n$ ), and the sum  $\text{SO}_2 + \text{H}_2\text{S}$  [5]. This sum could be practically considered as sulfurous acid, since hydrogen sulfide appeared only in traces. Elementary sulfur did not form at all during the hydrolysis of sulfur dichloride in Gil-Beato's solution.

TABLE 1

Hydrolysis of Sulfur Dichloride in Gil-Beato's Solution

Expt. No.	1		2		3	
Used (milli-moles):						
$\text{SCl}_2$	9.34		8.65		11.44	
$\text{Na}_2\text{S}_2\text{O}_3$	15.41		19.32		27.75	
Time of analysis* (in min)	60		30		30	
Reaction products	Milli-moles	% S**	Milli-moles	% S**	Milli-moles	% S
$\text{H}_2\text{S}_2\text{O}_3$	0.10	0.5	1.85	7.8	4.72	14.1
$\text{SO}_2$	2.07	5.1	1.55	3.3	2.10	3.1
$\text{H}_2\text{S}_n\text{O}_6$	7.27	91.6	8.86	93.7	11.52	87.3
$n$	5.06		5.0		5.08	
Consumption $\text{H}_2\text{S}_2\text{O}_3$ : $\text{H}_2\text{S}_n\text{O}_6$ found	2.1:1		1.97:1		2.0:1	

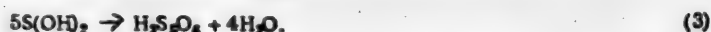
Table 1 gives the results of several experiments in which 1.65 to 2.4 moles of thiosulfate were used for 1 mole of sulfur dichloride. The analysis of the mixture was conducted almost immediately after the disappearance of the sulfur dichloride.

It is apparent from the results given that the main reaction product is pentathionic acid, in which form 90% and more of the sulfur used is found. The ratio of the number of molecules of reacted thiosulfate to

the number of molecules of polythionic acids formed was close to 2:1 in all cases as required by the equation:



In experiments 2 and 3, the number of millimoles of pentathionic acid found is also close to the number of millimoles of sulfur dichloride used. The deviation from these results in experiment 1 is explained by the fact that some excess sulfur dichloride was used here, as a result of which part of the hydrosulfurous acid was converted into pentathionic acid in the same manner as with the hydrolysis in the absence of thiosulfate [6]; i.e., according to the general equation:



This explanation was confirmed by the fact that the starting thiosulfate reacted almost completely in experiment 1, whereas in both of the other experiments, in which a small excess of thiosulfate based on the ratio  $\text{SCl}_2$ : $\text{Na}_2\text{S}_2\text{O}_3 = 1:2$  was used, this excess remained unused.

Therefore, it follows from these experimental results that the hydrolysis of sulfur dichloride in Gil-Beato's solution leads to practically a quantitative formation of pentathionic acid according to equation (2).

A phenomenon, which appeared strange at first, was observed upon repeating these experiments. It was frequently found that the number of moles of polythionic acid formed was considerably less than the starting number of moles of sulfur dichloride, but the average number of sulfur atoms in the molecules of these acids ( $n$ ) was found to be much higher than five in these cases. Therefore, in such experiments, in addition to pentathionic acid, hexathionic and other higher polythionic acids must have been formed. Table 2 gives the results of two such experiments with "anomalous" results.

The fact must be kept in mind that the consumption of thiosulfuric acid for 1 mole of polythionic acid is considerably greater than 2 moles in these experiments. This fact leads to the conclusion that hexathionic acid is formed as a result of the secondary reaction:



\* From the start of the sulfur dichloride hydrolysis.

\*\* The sulfur used is taken as 100%.

TABLE 2

"Anomalous" Results of the Hydrolysis of Sulfur Dichloride in Gil-Beato's Solution

Expt. No.	4		5	
Used (millimoles):				
SCl <sub>2</sub>	8.76		11.43	
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	17.0		24.42	
Time of analysis (in hrs)	2		1	
Reaction products	Milli-moles	% S	Milli-moles	% S
H <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	2.61	12.8	2.65	9.1
SO <sub>2</sub>	3.63	8.9	3.21	5.5
H <sub>2</sub> S <sub>n</sub> O <sub>6</sub>	5.58	78.1	8.68	83.7
n	5.7		5.6	
Consumption H <sub>2</sub> S <sub>2</sub> O <sub>3</sub> : H <sub>2</sub> S <sub>n</sub> O <sub>6</sub> found	2.58:1		2.51:1	

ous acid does not occur with sufficient speed, and the thiosulfuric acid found in the solution is practically consumed for the sulfuration of the pentathionic acid already formed according to (4), instead of according to equation (2) for the formation of pentathionic acid.

In order to prove this explanation for the formation of hexathionic acid; i.e., reality of reaction (4), the change of the composition of the reaction mixture with time was determined in the subsequent experiments. In experiment 6 (Table 3), analyses conducted a half hour after the start of the hydrolysis of sulfur dichloride showed a "normal" composition of reaction products; i.e., analogous to those obtained in experiments 1-3. Analysis conducted after 2.5 to 5 hours showed that polythionate sulfur and the average number of sulfur atoms in the polythionic acid molecules (n) increased with time because of the remaining thiosulfuric acid. Therefore the existence of the secondary sulfuration reaction of pentathionic acid according to equation (4) cannot be disputed.\*

TABLE 3

Expt. No. 6. Change of the Composition of the Hydrolysis Products of 9.33 Millimoles of SCl<sub>2</sub> in a Gil-Beato's Solution Prepared from 22.65 Millimoles of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

Time from beginning of hydrolysis	30 minutes	2.5 hours	5 hours
% S in form of H <sub>2</sub> S <sub>n</sub> O <sub>6</sub>	89.4	91.9	93.6
n	5.05	5.08	5.12
% S in form of H <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	10.4	9.6	7.2

the hydrolysis of sulfur dichloride, and then several hours later. The results in Table 4, as well as their comparison with those of previous experiments (for example, 2, 3, and 6), show that the average number of sulfur atoms in the polythionic acid molecule (n) is higher, the greater the excess of thiosulfate used based on the ratio Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>:SCl<sub>2</sub> = 2:1. This number also increases considerably with time which is accompanied by the consumption of thiosulfuric acid and an increase in the amount of sulfur dioxide in the solution. Therefore, these experiments also prove that the formation of the higher polythionic acid occurs according to equation (4).

The use of 3 moles of thiosulfate for 1 mole of sulfur dichloride (experiment 7) gives a solution whose analysis after 3.5 hours at 0° reveals that hexathionic acid with a small impurity of unreacted thiosulfuric acid and sulfur dioxide was present.

\*The possibility of the formation of hexathionate from pentathionate according to equation (4) has been questioned by several authors [7].

The great difference between the "anomalous" results of these experiments and the results of experiments 1-3 is explained by the heterogeneous process of the hydrolysis of sulfur dichloride. Sulfur dichloride is not miscible with aqueous solutions, and the formation of hydrosulfurous acid occurs on the interfacial surface between the liquid phases. For this reason its rate of formation depends upon factors very difficult to control, like the rate of mixing and the size of the interfacial surface between the phases. Since hydrosulfurous acid reacts extremely rapidly under these conditions, which is shown by the fact that almost no auto decomposition occurs, which is usually accompanied by the precipitation of sulfur [1], the rate of formation of pentathionic acid according to (2) must depend mainly upon the rate of the heterogeneous process of hydrolysis of sulfur dichloride. It can be supposed that, for example, with an insufficiently efficient shaking of the reaction mixture, the formation of hydrosulfur-

The results led to the idea of using the hydrolysis of sulfur dichloride in a Gil-Beato's solution for the preparation of hexathionic acid. Since the latter is formed by means of the reversible reaction (4), an excess of thiosulfuric acid must shift this equilibrium to the right. For this reason, in subsequent experiments, the starting ratio of thiosulfate:sulfur dichloride was changed to 3:1 and 4:1 (experiments 7 and 8, Table 4).

In both experiments, the analysis was initially conducted at practically the end of

TABLE 4

Hydrolysis of Sulfur Dichloride in the Presence of Thiosulfuric Acid

Expt. No.	7				8			
Used (m-moles)								
SCl <sub>2</sub>	10.36				13.38			
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	30.18				52.0			
Time of analysis	30 minutes		3.5 hours		30 minutes		2 hours	
Reaction products	Milli-moles	% S	Milli-moles	% S	Milli-moles	% S	Milli-moles	% S
H <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	5.64	15.9	4.97	14.0	8.27	14.2	6.81	11.7
SO <sub>2</sub>	5.61	7.9	6.83	9.6	17.69	15.1	20.0	17.1
H <sub>2</sub> S <sub>n</sub> O <sub>6</sub>	9.25	74.0	8.80	74.2	13.77	72.3	13.34	72.0
n	5.68		5.99		6.13		6.3	

Increasing this ratio to 4:1 (experiment 8), results in a solution of practically analogous composition at once; i.e., during the first analysis, which was conducted a half hour after the start of hydrolysis. Two hours later, a considerable amount of heptathionic acid, and possibly other acids with  $n \geq 6$  were present.

The formation of higher polythionic acids; i.e., with  $n \geq 6$ , from sulfur dichloride and thiosulfate has been unreported in the literature up to now.

The authors were not satisfied with the analysis of the solution obtained, which showed the presence of higher polythionic acids, and made a series of attempts to obtain these acids as benzidine salts. The procedure used was analogous to that reported in one of the previous communications. The precipitates obtained by the addition of a benzidine hydrochloride solution to the reaction mixture were usually recrystallized from 1N hydrochloric acid and dried at room temperature in a desiccator. A short characterization of the preparations obtained is given in Table 5.

TABLE 5

Analysis of Benzidine Polythionates

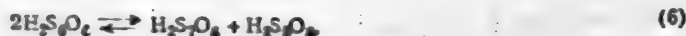
Preparation No.	% S, found	% S calculated according to the formula	Notes
1	43.8	44.3 Bz H <sub>2</sub> S <sub>7</sub> O <sub>6</sub> *	Used Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> :SCl <sub>2</sub> = 3.9:1
2	44.2		Fraction I precipitate, recrystallized
3	50.0	50.5 Bz H <sub>2</sub> S <sub>7</sub> O <sub>6</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> :SCl <sub>2</sub> ≈ 3:1;
4	45.8	47.5 Bz H <sub>2</sub> S <sub>7</sub> O <sub>6</sub>	Fraction I recrystallized
5	37.6	36.3 Bz H <sub>2</sub> S <sub>9</sub> O <sub>6</sub>	" " not recrystallized
6	37.3		" " recrystallized
			Fraction II, after removal of preparation 4; recrystallized.
			Fraction II, recrystallized.

found for considering these preparations to correspond to individual compounds; rather there is an inclination to regard them as mixtures, because they could not be reproduced.

However, these experiments do not leave any doubt that higher polythionic acids are formed upon the hydrolysis of sulfur dichloride in Gil-Beato's solution containing an excess of thiosulfuric acid. Their formation can be expressed, considering the presence of acids with  $n > 6$  in the solutions, by the general equations:



In addition the redistribution reaction of sulfur between the molecules of polythionic acids [8] is very probable; for example, according to the equation:



\* Bz = C<sub>12</sub>H<sub>8</sub>(NH<sub>2</sub>)<sub>2</sub>

The analytical results show that Fraction I of the precipitate formed by benzidine, contains polythionates with 7-9 sulfur atoms in the molecule; pentathionate predominates in Fraction II. The composition of preparation No. 2 very nearly corresponds to the formula for the heptathionate; preparation No. 3 is close to nonathionate. However, sufficient basis was not

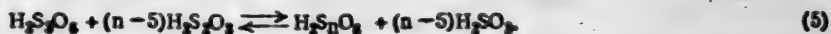


## SUMMARY

1. Hydrolysis of sulfur dichloride in Gil-Beato's solution led very rapidly and practically quantitatively to the reaction of hydrosulfurous acid with thiosulfuric acid according to the equation:



2. The use of an excess of thiosulfate based on the ratio  $\text{Na}_2\text{S}_2\text{O}_3 : \text{SCL}_2 = 2:1$  made possible the formation of higher polythionic acid solutions under these conditions. These acids were formed from pentathionic acid as a result of the reaction:



3. Benzidine polythionates were obtained whose composition varied between heptathionate and nonathionate.

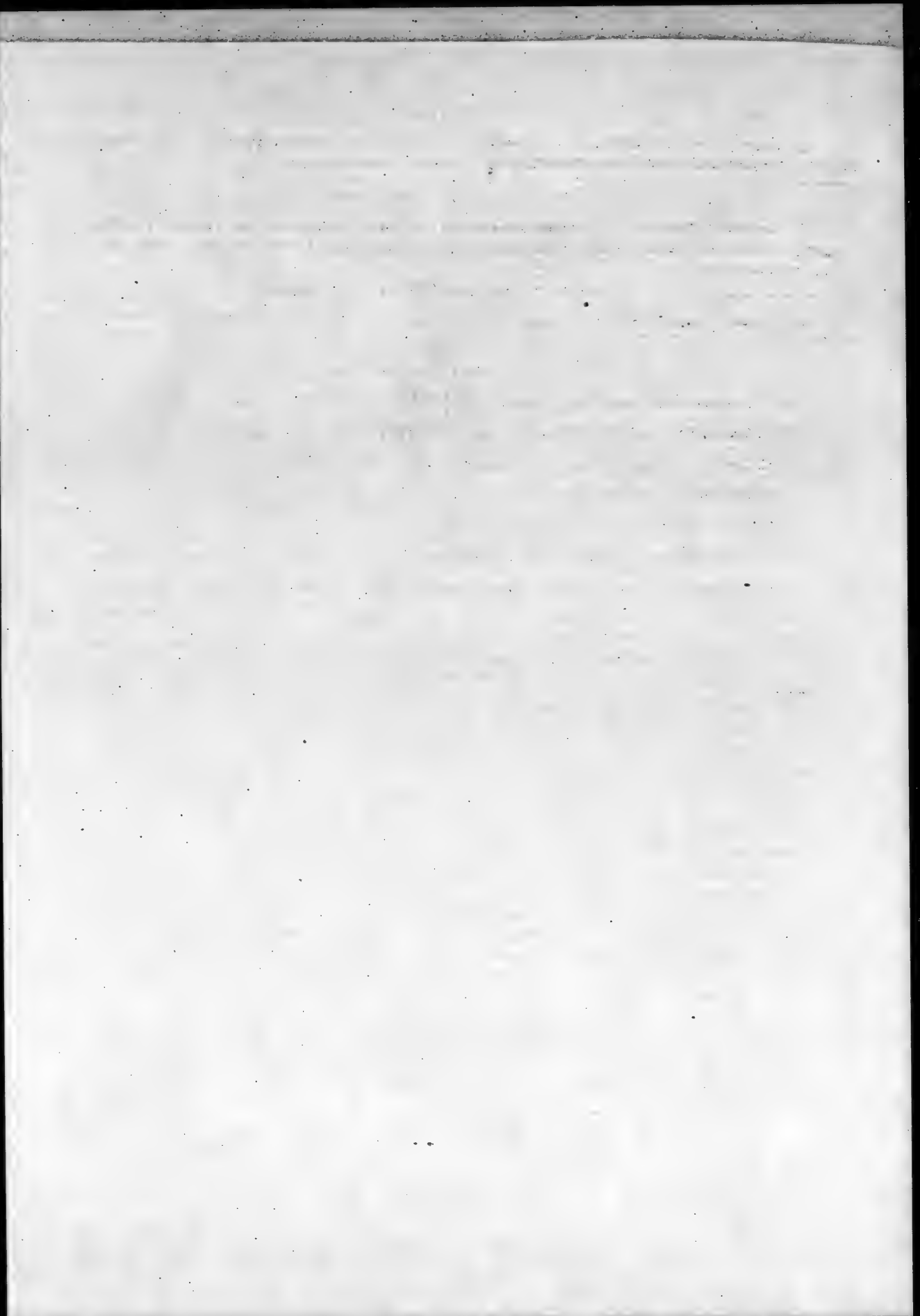
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Received April 6, 1953

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\* See Consultants Bureau Translation, page 1509.



## INVESTIGATION OF THE SYSTEM PLATINUM-OXYGEN

### II. ENTHALPY OF FORMATION OF PLATINIC OXIDE $\text{Pt}_2\text{O}_4$

S. M. Ariya, M. P. Morozova, and A. A. Reikhardt

Establishment of the homogeneity of the product of the oxidation of platinum with oxygen made possible the start of the study of the thermodynamics of this compound. The reaction of platinic oxide with hydrogen was chosen in order to establish the enthalpy of its formation.\*



This reaction starts the moment of contact between hydrogen and platinic oxide at room temperature; it does not require any catalysis and proceeds rapidly. Platinum is obtained in the form of grey powder, i.e., with small specific surface, which excludes any possibility of distorting the value of the thermal effect because of the heat of adsorption of the hydrogen on the surface of the metal. The completeness of the reduction of the oxide under these conditions was established experimentally. Therefore, the reduction reaction of  $\text{Pt}_2\text{O}_4$  with hydrogen satisfies the requirements of reactions that are to be effected in a calorimeter.

The calorimetric vessel was a brass cylinder with a ground brass cover. A heater (a copper ring wound with constantan wire) was placed in the center within the cylinder. A glass ampoule containing a sample of the preparation (0.25g-0.45g) weighed on an analytical balance with an accuracy of 0.2 mg, from which the air was removed until a residual pressure of  $10^{-4}$  mm, was suspended after sealing, from the cover of the vessel with tungsten threads. The calorimetric vessel was hermetically sealed and evacuated through a small vacuum stopcock placed in the cover of the vessel to the above residual pressure. The hydrogen, completely purified from oxygen, was introduced into the calorimetric vessel with sufficient moisture in it to saturate it with water vapor. The center of the cover had a cavity in which a thermal resistor was placed.

The calorimetric vessel was suspended, insulated by the cover, in a sheath which was a hollow brass cylinder hermetically sealed with a cover to which tubes were connected for the exit of wires going to the thermal resistor, heater, and tungsten threads. A second auxiliary brass vessel was placed in this envelope, which served to decrease the heat exchange between the calorimetric vessel and its surroundings.

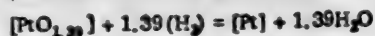
The hermetically sealed envelope was placed in about a 100-liter water thermostat in which were installed two stirrers, a heater, and thermoregulator by means of which, with the aid of a vacuum tube relay, the temperature of the thermostat was held at  $25 \pm 0.01^\circ$ . The resistance of the thermal resistor was measured with a Wheatstone bridge (Balon). A Siemens mirror galvanometer was used as the zero instrument. Upon using a subjective method, the reading could be made to an accuracy of 0.1 ohm. A change in the temperature of  $1^\circ$  corresponded to a change of the resistance of 209 ohms, i.e., 0.1 ohm corresponded to a change of temperature of 0.0005°. The strength of the current in the thermal resistor was only of the order of 0.0004 A, which made it possible to neglect the energy separating from it.

Before the start of each series of experiments, the presence of a linear relationship between the uncompensated bridge and the deviation of the mirror of the galvanometer was determined. When the calorimetric vessel attained a temperature of  $24.5^\circ$ , a measurement of the resistance of the thermal resistor was conducted in 30-second intervals. If the changes of the resistance were equal during 12-15 measurements, then the tungsten wire on which the ampoule with the preparation hung, was melted. Falling, the ampoule was broken on the bottom of the vessel, and the preparation reacted with the hydrogen.

The increase of the temperature at the time of the experiment with the platinic oxide was compared with the increase of the temperature which occurred when energy was introduced into the calorimetric vessel by the passage of a current across the heater. The fall of the resistance on ends of the heater was measured potentiometrically. The correction for the heat exchange of the calorimetric vessel with the surroundings was introduced by the Reniot-Pfaundler equation [2]. The correction was from 1.5-7%.

\* The same reaction, reduction of the oxide, was used by Wöhler [1] for the determination of the enthalpy of formation of  $\text{PdO}$ .

On the basis of the above reported measurements of the enthalpy of the reaction



the enthalpy of formation of the oxide of this composition was found to be equal in a series of experiments, to: -14.7, -13.0, -12.9, -13.6, -14.0, and 13.3 kcal. Therefore,  $-13.6 \pm 1.1$  kcal. is obtained as an average for the enthalpy of formation of



The temperature relation of the value of the oxygen pressure, corresponding to the equilibrium

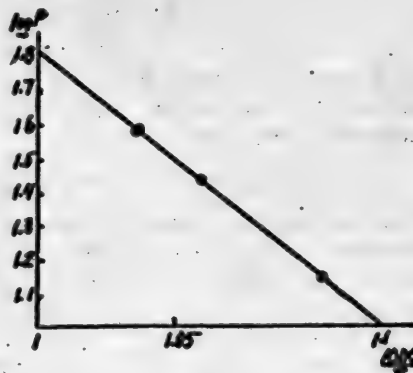


was investigated.

The values obtained are given in the Table.

Temperature	Equilibrium pressure of oxygen (in kg/cm <sup>2</sup> )
650°	14.2
680°	27.6
700	37

The Figure gives the relation of the logarithm of the dissociation elasticity of platinum oxide to the inverse value of the absolute temperature. All three points, as the Figure shows, satisfactorily fit on a straight line.



Considering the change of enthalpy and entropy of this process approximately constant at 650-700°. It is found (using the generally known thermodynamic equation  $RT \ln K = \Delta H - T\Delta S$ ) correspondingly,

$$\Delta H_{650^\circ\text{C}} = 11.5 \text{ kcal and } \Delta S_{650^\circ\text{C}} = 43.1 \text{ kcal/}^\circ\text{C}$$

The enthalpy of formation of the oxide at room temperature must be somewhat higher (in absolute value), i.e., the value found by tensiometric results confirms that obtained calorimetrically.

The enthalpy of formation of nickel and palladium oxides, analogs of platinum in the vertical column of the periodic system, are higher in absolute value, namely for NiO = -58.4 kcal, for PdO = -20.4 kcal.

Nickelous oxide has considerably different properties from palladium and platinum oxides which can be assigned to the metal-like oxides (they possess, for example, in contrast to NiO, a high metallic electroconductivity), while nickelous oxide resembles the salt-like oxides. It is natural, for this reason, to compare the values of the enthalpy of formation of PdO and  $\text{PtO}_{1.39}$ .

Previously it was stated that an oxide, close in composition to the formula  $\text{Pt}_2\text{O}_3$ , is the only thermodynamically stable phase in the system platinum-oxygen\*. In other words, the process of disproportionation of the hypothetical oxide PtO



must be accompanied by a decrease of free energy. Since only solid phases participate, the change of entropy can be neglected, and with a good degree of accuracy, it can be considered that PtO disproportionates because of the exothermic nature of the above-given reaction. In other words, the heat of formation of PtO must be less than +28 kcal/mole (the heat of formation of  $0.72 \text{ PtO}_{1.39}$ ). In addition, this value, in all probability, is greater than zero, i.e., it can be supposed that it is confined to the interval 0-10 kcal.

If the enthalpies of formation of PdO and PtO are calculated from oxygen in its standard state and from mono-atomic vapors of the metals (enthalpy of vaporization of Pd is 110 kcal, Pt, 127 kcal [4], the following values are

\* Recently [3] a paper by Galloni and Busch appeared in which the authors also came to the conclusion that the existence of PtO reported by a series of authors, must be doubted.



obtained:



If it is considered that the enthalpy of vaporization of the above metals, actually, is determined without sufficient accuracy, both values may be considered practically equal, i.e., in other words, the decrease of stability of oxides upon going from palladium to platinum is mainly due to the increase of stability of the metallic lattice in this direction.

#### SUMMARY

##### 1. The enthalpy of the reaction



was determined calorimetrically; the value of the enthalpy of formation of platinic oxide was found to be:

$$\Delta H_{\text{formation PtO}_{1.39}} = -13.6 \pm 1.1 \text{ kcal.}$$

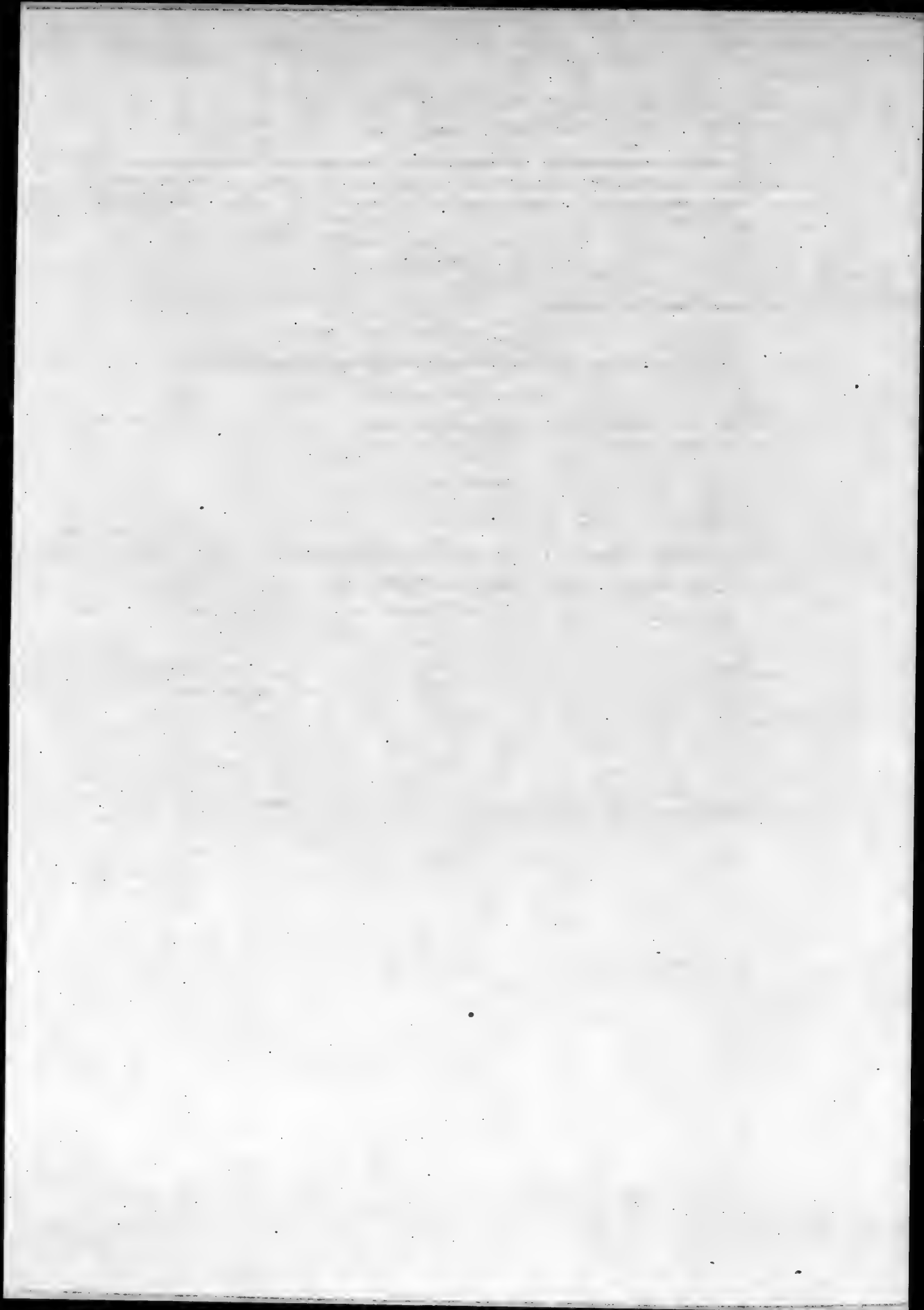
2. The above value agrees with the results of the investigation of the equilibrium of the process of dissociation of platinic oxide.

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Received November 1, 1952

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## TERNARY COMPLEXES IN THE SYSTEM COPPER IONS-PYRIDINE-SALICYLATE

### II. RELATION OF THE COMPOSITION OF THE COMPLEXES TO THE pH OF THE SOLUTION

A. K. Babko and M. M. Tananaiko

During the reaction of cuprous ions with pyridine and salicylic acid, the formation of poorly soluble complex compounds occurs, which are readily extractable by non-aqueous solvents. Chloroformic extracts of the complex are colored intense blue, and for this reason, the reaction is used for the colorimetric determination of copper [1] and salicylic acid [2].

There is data in the literature on pyridine salicylate complexes of the composition  $\text{CuPy}_2\text{Sal}_2$  [3], as well as  $\text{CuPy}_2\text{Sal}_2 \cdot 2\text{CuPy}_2\text{Sal}$ ;  $2\text{CuPy}_2\text{Sal}_2 \cdot \text{CuPy}_2\text{Sal}$  [4]. These complexes were isolated in solid form by mixing solutions of the corresponding amounts of the starting substances. Any relationship of the equilibrium in aqueous solution to the pH of the solution, etc., was not established by these authors; the question of the structure of these complexes also were not discussed.

In 1948, one of the authors of the present communication [5] studied the complex formation in the system copper ions-pyridine. A method for the physico-chemical analysis of a system with three reaction components in solution was developed. The results of the investigation showed the formation of the ternary complex  $\text{CuPy}_2\text{Sal}$  in the system, stable at known limits of concentration, in which the copper is coordinately attached to the pyridine and salicylate ion. Later, the equilibrium between the reaction components in the above system was studied [6].

A more detailed investigation, the results of which are reported in the present communication, led to the conclusion that the reaction of copper with pyridine and salicylate resulted in the formation of several ternary compounds of various composition.

Salicylic acid, which enters into the composition of the copper pyridine salicylate complex, is a weak acid. Its degree of dissociation, and correspondingly, participation in complex formation to a considerable extent depend on the acidity of the solution. For this reason, complex formation in the system copper ion-pyridine-salicylate was studied in relation to the pH of the medium. The investigation was conducted on the basis of the change of the optical characteristics of the solutions. Since the copper pyridine-salicylate complexes were readily soluble in non-aqueous solvents, chloroformic extracts, as well as aqueous solutions were studied.

#### Spectral Characteristics of the Solutions

Absorption spectra of the copper pyridine-salicylate complex were studied at various pH's. The optical densities of aqueous solutions and chloroformic extracts were measured. The measurements of the light absorption values of the extracts directly characterized the ternary complex, since the secondary copper complex with pyridine, as well as copper with salicylic acid, was not extractable with non-aqueous solvents [5].

The acidity of the medium was changed by the addition of 0.1 N sodium hydroxide or 0.1 N nitric acid\*. To conduct this experiment, 2 ml of 0.05 M copper nitrate solution, 4 ml of 0.05 M pyridine, and 4 ml of 0.05 M sodium salicylate were mixed together in test tubes. After mixing, acid or base was added to the solution. The solutions were mixed, and their optical densities were measured on the FM photometer.

Another series of analogously prepared solutions was shaken with 5 ml of chloroform, and the light absorption of the obtained extracts was measured. Parallely, the pH was measured with a vacuum tube potentiometer of the LP-4 type with quinhydrone electrodes. The absorption spectra obtained as a result of the investigation are given in Figs. 1 and 2.

\* Buffer solutions were not used since the substances entering into their composition could have affected the complex formation.

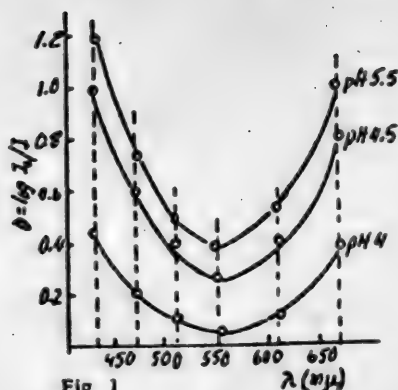


Fig. 1

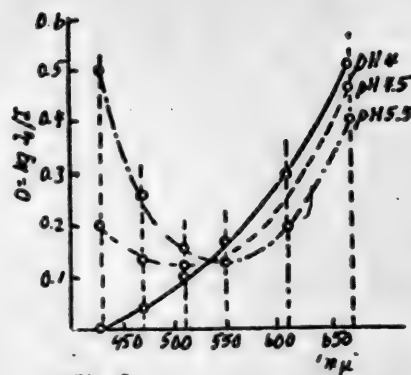


Fig. 2

As it is apparent (Fig. 1) in aqueous solutions, increase of pH does not affect the character of the light absorption of the solutions, but only results in the increase of the optical density. All of the solutions were green in color, and intensely absorbed in the red and violet parts of the spectrum. A formation of a precipitate occurs at  $\text{pH} > 6$ .

The more characteristic absorption spectra of the chloroformic extracts is given in Fig. 2. In this case, some decrease of light absorption in the red and a strong increase in the violet parts of the spectrum occur upon increasing the pH of the aqueous phase. Correspondingly, the color of the extracts goes from blue to yellow.

At pH of 4 to 4.5 in the aqueous phase, a blue colored compound is extracted. At pH of 5 to 5.5, the color of the extracts becomes green. At  $\text{pH} > 6$  the amount of the substance extracted decreases without change of the character of light absorption.

On the basis of the results obtained, it may be concluded that the reaction of copper with pyridine and sodium salicylate leads to the formation of two ternary complexes having the same color in the aqueous phase, but different colors in non-aqueous solvents. In more acidic media, (pH 4-4.5), a blue colored compound is formed; at pH 5-5.5, the formation of a complex having a green color in chloroform occurs.

Further increase of pH ( $\text{pH} > 6$ ), as it was shown previously [6], leads to the disruption of the ternary, and the formation of the more stable copper disalicylate complex  $\left[ \text{Cu} \left( \begin{array}{c} \text{O} \\ \text{OOC} \end{array} > \text{C}_6\text{H}_4 \right)_2 \right]^2$ , which is not extractable with non-aqueous solvents.

#### Physico-Chemical Analysis of the Solutions

The physico-chemical analysis of the system copper-pyridine-salicylate was conducted with two series of solutions. In the first series, conditions were created which favored the formation of the complex having a blue color in the non-aqueous phase. For this reason, starting solutions with pH 4 to 4.5 were prepared. In the second series, alkali was added to  $\text{pH} \sim 5.5$  to analogous solutions in order to obtain compounds which extracted green. 0.05 M solutions of copper nitrate, pyridine, and sodium salicylate were used for the investigation. The solutions were mixed at various ratios, but in such a manner that the volume of all three components was always constant and equal to 10 mL.

Thus, for example, solutions corresponding to points 1-10 on the triangle diagram in Fig. 3, were prepared by the mixing of 1, 2, 4, ..., 10 ml of 0.05 M  $\text{Cu}(\text{NO}_3)_2$  with 9, 8, 6, ..., 0 ml of 0.05 M pyridine. Solutions, corresponding to points lying within the triangle diagram, were prepared by mixing all three components. For example, the solution, corresponding to point 36, was prepared by mixing 2 ml of 0.05 M copper nitrate, 4 ml 0.05 M, pyridine, and 4 ml of 0.05 M sodium salicylate.



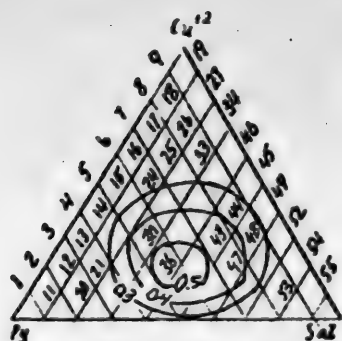


Fig. 3.

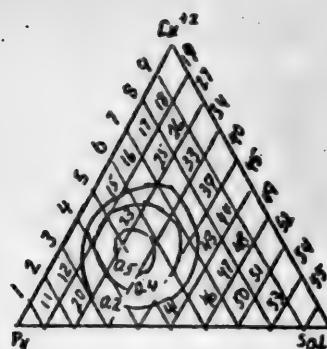


Fig. 4.

The measurements of the light absorption of the aqueous solutions were conducted with two light filters having an effective wavelength of 670 and 430 mμ respectively. Judging by the data in Figs. 1 and 2, the most characteristic results could be expected in these parts of the spectrum. The optical density of solutions of the ternary complex in chloroform was studied in supplementary experiments for each series. 10 ml of the aqueous solution was shaken with 5 ml of chloroform, and the optical density of the extracts obtained was measured. The method for processing the results remained the same as in the previous communication [5]: binary diagrams were constructed on the basis of the values of the absorption found, which were sections through the triangle diagram (Fig. 3) with lines parallel to the side Cu-Py. Points on Fig. 3 corresponding to compositions having identical absorption values, were sought from the data of the binary diagrams. Isochromes were obtained by joining these points with lines.

Fig. 3 gives the isochromes obtained by measurement of the optical density of chloroformic extracts at pH 4-4.5 in the aqueous phase. From the form of the isochromes, it can be concluded that the maximum optical density corresponds to a ratio of Cu:Py:Sal = 1:2:2.

In the second series of experiments, measurements were conducted analogously but with this difference: sodium hydroxide was added to the solutions until the transition of the color of the chloroformic extract from blue to green. It was found empirically that 2 ml of 0.1 N alkali was sufficient under the above reported conditions. As shown experimentally, the pH of the solutions was about 5.5. Fig. 4 gives the isochromes obtained by measuring the optical density of green chloroformic extracts. As it is apparent from the data of this figure, the maximum absorption corresponds to a ratio of Cu:Py:Sal = 1:2:1. Analogous results were obtained by the measurement of the optical density of aqueous solutions.

Therefore, physico-chemical analysis of the system led to the conclusion that the complex  $\text{CuPy}_2\text{Sal}_2$  was formed at pH 4.5. At pH 5.5, the formation of the complex  $\text{CuPy}_2\text{Sal}$  occurs.

Because the above complexes were sufficiently poorly soluble in water, they were isolated in the solid phase. Precipitates were obtained by the treatment of 10 ml of a 0.1 M solution of copper nitrate with a mixture of 10 ml 1 M sodium salicylate and 10 ml 1 M pyridine at various acidity. The treatment of a copper nitrate solution with the precipitating mixture with the addition of 0.5 ml of 0.1 N nitric acid led to the formation of a white powdery residue. If 1 ml of 0.1 N sodium hydroxide was initially added to the precipitant, a green flocculant precipitate of copper pyridine salicylate formed. The residues were filtered, washed with cold water, and dried at room temperature between sheets of filter paper.

It was shown experimentally that the blue residue dissolved in chloroform with the formation of a blue solution. The green residue gave a green chloroformic extract.

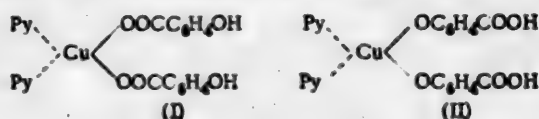
In order to confirm the composition of the complexes, the copper content was determined in the preparation obtained. The copper was analyzed electrolytically. The analytical results are given in the Table.

	Sample (g)	Cu found (g)	Cu found (%)	Cu calculated (%)
Blue complex .....	0.20	0.0262	13.1	CuPy <sub>2</sub> Sal <sub>2</sub>
	0.50	0.0628	12.1	Cu - 12.82
Green complex .....	0.10	0.0180	18.0	CuPy <sub>2</sub> Sal
	0.15	0.0270	18.0	Cu - 17.78
	0.20	0.0362	18.1	

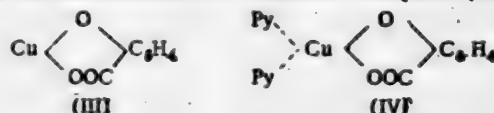
As it is apparent from the data in the Table on the determination of copper, the blue complex corresponds to the composition CuPy<sub>2</sub>Sal<sub>2</sub>, and the green - CuPy<sub>2</sub>Sal.

Salicylic acid, which enters into the composition of the copper pyridine-salicylate complex, can dissociate with the cleavage of hydrogen of the carboxylic group, or of the hydroxyl group. For this reason, several structures can be suggested for the ternary complexes formed.

Structures (I or II) can be suggested for the structure of blue complex CuPy<sub>2</sub>Sal<sub>2</sub> in which the copper substitutes the carboxylic hydrogen, or that of the hydroxyl group of the acid:



Upon the increase of the pH, the substitution of the other hydrogen atoms (hydroxylic or carboxylic groups of salicylic acid) is facilitated, and the formation of a "chelated" compound (III) • can occur



which reacting with pyridine, forms the green complex (IV).

To solve the problem of the structure of the ternary complexes, supplementary experiments on the investigation of the extractability of the copper complexes with pyridine and methyl salicylate, as well as of the first two compounds with methoxybenzoic acid, were conducted.

It was shown experimentally that compounds were formed by the reaction of copper with pyridine and methoxybenzoic acid, which gave blue chloroformic extracts. The complex with pyridine and methyl salicylate was extracted with the formation of a green extract. Acidification of the solutions led to the decomposition of the complexes and the decolorization of the non-aqueous phase. Upon making the solutions alkaline, the blue complex was decomposed, while the green remained stable even in 1 M alkali solutions. ••

From the results obtained, it could be concluded that the copper is bound to the carboxylic group of salicylic acid in the blue complex CuPy<sub>2</sub>Sal<sub>2</sub> (Structure I), since the formation of a compound giving a green chloroformic extract could be expected with the presence of a bond across the hydroxyl group. The formation of green extracts by the complex CuPy<sub>2</sub>Sal, without doubt, can be explained by the presence of a bond of copper with the OH group of salicylic acid in this compound in addition to that with the carboxylic group.

• Another suggestion for the complex CuPy<sub>2</sub>Sal, apparently cannot be made, since, if copper substituted only one of the hydrogen atoms in salicylic acid, the formation of (at a ratio of Cu : Sal = 1:1) a single charged cation would have occurred, which could not be extracted, since it cannot form a neutral molecule with the PyH<sup>+</sup> pyridine cation, as well as form a molecule with molecular pyridine.

•• The stability of the complex of copper with pyridine and methyl salicylate is aided, evidently, by the absence of possibility for transition to copper disalicylate [CuSal<sub>2</sub>]<sup>-2</sup>, which occurs for the corresponding complex of copper with salicylic acid.

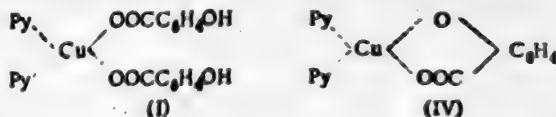
Therefore, the investigation of the optical characteristics of the solutions, analysis of the solid substances, and the study of the extractability of complexes of copper with pyridine and certain derivatives of salicylic acid, lead to the conclusion that the reaction of copper with pyridine and salicylic acid leads to the formation of several compounds. Complex (I), in which the copper is bound to the carboxylic group of the acid, is formed in more acidic solutions which hinder the dissociation of the hydroxyl group. By increasing the pH, the substitution of the OH group hydrogen of salicylic acid is facilitated, which leads to the formation of complex (IV), in which copper is bound to the carboxylic and the hydroxyl groups of the acid. Increase of pH to  $>8$  leads to the decomposition of the ternary complexes, and the formation of the more stable copper disalicylate [4].

Of the two pyridine-salicylate copper complexes, the blue one,  $\text{CuPy}_2\text{Sal}_2$ , is more soluble in non-aqueous solvents, because of which it can be successfully applied for the separation of copper from cations which do not form extractable pyridine salicylate complexes.

#### SUMMARY

The complex formation in the system copper ion-pyridine-salicylate was studied in relation to the acidity of the solution. Methods of physico-chemical analysis of colored ternary complexes in solution were used for the investigation. The optical density of the aqueous solutions, as well as the absorption of the chloroformic extracts, were the properties measured.

It was found that at pH of the aqueous phase from 4 to 4.5, ternary complex (I) was formed; while at pH 5 - 5.5 the formation of complex (IV) occurred:



The data on the composition of the complexes were confirmed by the isolation of solid compounds, as well as the study of certain derivatives.

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Received April 16, 1953.

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# OXIDATION OF ALCOHOLS BY THE EFFECT OF ULTRASONIC FREQUENCIES

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It is known that ultrasound causes oxidation reactions in pure water and in aqueous solutions [1-5]. The decomposition of starch, inulin, agar-agar, as well as intense chemical changes in the monomers — glucose, fructose, galactose, and maltose, caused by sound, accompanied by the formation of acids and aldehydes [6, 7].

The action of ultrasonic frequencies leads to the decomposition of polypeptide chains and formation of ammonia and aldehydes in solutions of gelatin [8]. Amino acids are also subject to chemical change by this treatment. The available data indicates that cavitations formed by the action of ultrasonic vibrations cause the activation of oxygen, dissolved in the liquid, and the decomposition of water with the formation of free radicals and hydrogen peroxide [9, 10]. It was shown that the effect of ultrasonic vibration was similar to the action of ionizing radiation [11].

Because of the study undertaken on the effect of ultrasound on chemical processes [6-8, 12] it appeared of great interest to elucidate more fully the character of the oxidation reactions occurring under the influence of ultrasonic vibrations. For this reason, aqueous solutions of methyl alcohol and other alcohols, as well as various organic substances in methyl alcohol were subjected to sonation.

A high frequency oscillator described in previously published investigations [8], served for the preparation of ultrasonic vibrations. The strength of the oscillatory circuit was about 300-400 volts. The diameter of the piezo quartz plate was 50 mm. The frequency was 300 k-hertz/sec. The temperature of the solutions did not rise over 40° during the time of sonation. The solutions subjected to the action of ultrasound were placed, in 25 ml amounts, into conical vessels closed with stoppers during the experiment.

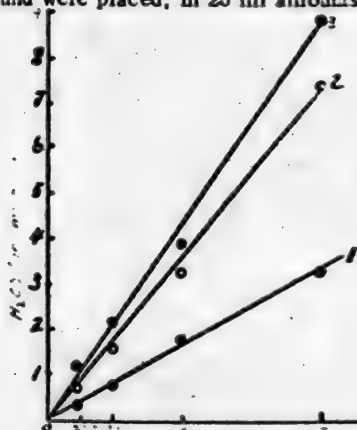


Fig. 1. Effect of sonation on the formation of formaldehyde in methyl alcohol solutions. 1) In 0.1% solution; 2) 0.5% solution; 3) in 1% solution.

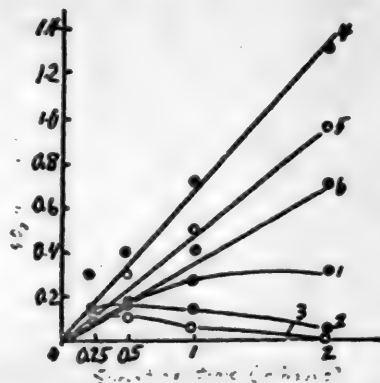


Fig. 2. Effect of sonation on the formation  $\text{NO}_2^-$  and  $\text{NO}_3^-$  in solutions of methyl alcohol. 1)  $\text{NO}_2^-$  in 0.1% solution; 2)  $\text{NO}_2^-$  in 0.5% solution; 3)  $\text{NO}_2^-$  in 1% solution; 4)  $\text{NO}_3^-$  in 0.1% solution; 5)  $\text{NO}_3^-$  in 0.5% solution; 6)  $\text{NO}_3^-$  in 1% solution.

Nitrous and nitric acids [13], and formaldehyde [14] were determined colorimetrically in the alcohol solutions immediately after the action of the ultrasound. Ammonia was determined by a diffusion method [15]. The experiments were repeated not less than 3 times. Pure preparations of alcohols and triply distilled water were used for the preparation of the solutions. After a 2 hour sonation, 0.104 mg of  $\text{NO}_2^-$ , 1.58 mg of  $\text{NO}_3^-$ , and 1.99 mg of  $\text{H}_2\text{O}_2$  formed in 100 ml of such water.

During the calculation of the acids formed, the amount of alkali necessary for the titration of the water subjected to the action of ultrasound under these conditions, was subtracted from the total alkali consumed for the titration of the sonated solutions.

The results of experiments on the action of ultrasonic vibrations on 0.1-1% solutions of methyl alcohol are given in Figs. 1 and 2. The curves show that an increase of formaldehyde formation occurs with increase of the sonation time. In addition, nitrous and nitric acids, products of the oxidation of nitrogen of the air dissolved in the water, are formed; the concentration of the nitrous acid first increases; then, as a result of its further oxidation, it decreases. The concentration of nitric acid continuously increases with the time of sonation.

The amount of nitrous and nitric acids, as well as formaldehyde, varies not only with the sonation time (Figs. 1 and 2), but also with the concentration of the alcohol.

With the same sonation time, the higher the concentration of the alcohol (within the limits of 0.1 to 1%), the greater the amount of formaldehyde formed, and the less that of nitrous and nitric acids. A peculiar relationship of the formation of formaldehyde to the concentration of the alcohol occurs with greater concentrations of methyl alcohol. Fig. 3 shows that the amount of formaldehyde formed increases with the concentration of the alcohol in solution, and reaches its greatest value in a 10% alcohol solution. Upon further increase of the concentration of the alcohol, its oxidation slows down, and the formation of formaldehyde decreases. In 50% alcoholic solution, the amount of formaldehyde is only 0.2 mg/100 ml. A similar relationship of the aldehyde formed to the concentration of the alcohol subjected to the action of ultrasound was found for ethyl alcohol [16].

The results of the effect of ultrasound on solutions of methyl, ethyl, n-propyl, and n-butyl alcohol are given in the table. The concentration of the alcohols was 0.02 molar, the sonation time, 3 hours.

It is apparent from the Table that aldehydes, whose quantities are calculated on the aldehyde groups, formed after a 3 hour sonation of solutions of the alcohols, increase from methyl to butyl alcohol. At the same time, the formation of nitric acid increases from ethyl to butyl alcohol. Data given above show that the longer the hydrocarbon chain of the alcohol, the more actively is the latter oxidized in the ultrasonic pole.

Alcohol	Aldehyde group •	NO <sub>2</sub>	NO <sub>3</sub>
	(in mg per 100 ml of solution)		
CH <sub>3</sub> OH .....	5.80	Traces	0.96
C <sub>2</sub> H <sub>5</sub> OH .....	7.98	Traces	0.40
C <sub>3</sub> H <sub>7</sub> OH .....	16.5	None	0.20
C <sub>4</sub> H <sub>9</sub> OH .....	19.4	None	0.14

• Determined by iodometric titration.

The alcohol subjected to decomposition also has an effect on the oxidation of nitrogen dissolved in the liquid. It is apparent from the Table that the formation of nitric acid depends on the chain length of the alcohol. The longer the chain of carbon atoms, the more actively the alcohol prevents the oxidation of the dissolved nitrogen. The greater the amount of substances in the solution subjected to the oxidizing effect of ultrasound, the more strongly is the process of oxidation of each of these moderated.

The results obtained in this relation, which require further study, are illustrated by the sonation of alcoholic solution of aminoacetic acid (glycine), as well as solutions of glucose and lactose.

The data on the effect of glycine on the oxidations of the alcohol are shown in Fig. 4.

It is apparent from the curves in Fig. 4 that the presence of glycine decreases the oxidation of methyl alcohol. Thus, with the increase of the concentration of glycine, the formation of formaldehyde decreases and approaches a limit at a concentration of glycine of 0.04 molar.

The processes of oxidation occurring as a result of the action of ultrasound also cause the decomposition of the amino acids [8]. Ammonia is formed, and, as a result of its subsequent oxidation, nitrous and nitric acids are formed; for this reason the amounts of the latter are greater in the alcoholic glycine solutions than in solutions of

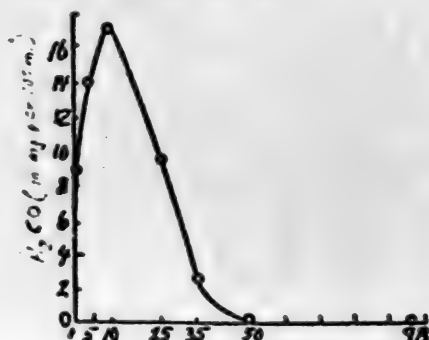


Fig. 3. Effect of the concentration of methyl alcohol on the formation of formaldehyde for a 2 hour sonation of the solutions.

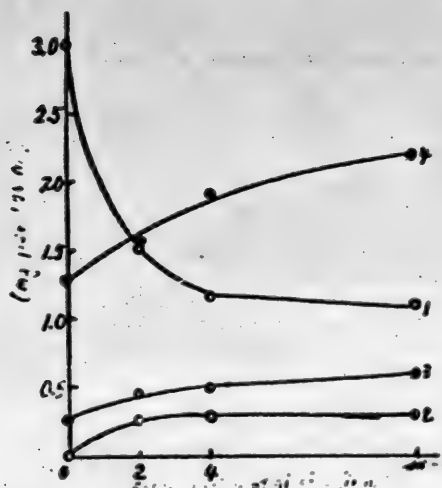


Fig. 4. Formation of  $\text{H}_2\text{CO}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{NH}_3$  in alcoholic solutions of glycine by the action of ultrasound. Concentration of methyl alcohol, 0.1%. Sonation time, 2 hours. 1)  $\text{H}_2\text{CO}$ ; 2)  $\text{NH}_3$ ; 3)  $\text{NO}_2^-$ ; 4)  $\text{NO}_3^-$ .

sonation of an 0.1% solution of methyl alcohol in which there was a mixture of glycine, glucose, and lactose each in concentrations of 0.02 molar, showed that the amount of formaldehyde formed under these conditions was 0.75 mg per 100 ml, i.e., less than in the presence of each of these substances alone.

The sugars themselves were subjected to oxidation by the action of ultrasonic vibrations [6, 7]. In the above reported experiments, 5.32 mg of COOH groups formed after a 2 hour sonation of an 0.1 M solution of glucose, which was 0.3% of the initial glucose (Fig. 5). The pH, equal to 6.66 initially, fell to 3.48 after the action of the ultrasound.

The product of the oxidation of methyl alcohol, formaldehyde, was subjected to further changes in the ultrasonic pole in relation to its formation.

It is apparent from the curves in Fig. 6 that the amount of formaldehyde decreases with the time of sonation of its solutions. Ultrasonic vibrations causing the oxidation of formaldehyde led to the formation of acids. After a 3 hour sonation, 1.82 mg of an acid, based on  $\text{HCOOH}$ , was formed in 100 ml of a formaldehyde solution. If a  $4 \cdot 10^{-2}$  molar concentration of glycine is added to the solution of the aldehyde, the oxidation of formaldehyde by the action of the sonation is slowed down.

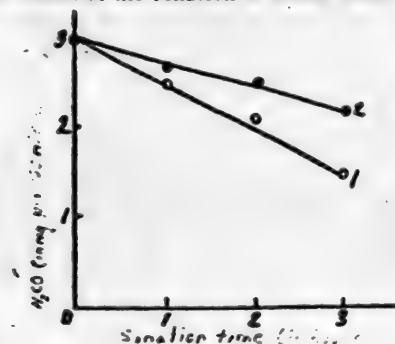


Fig. 6. Effect of sonation on solutions of formaldehyde. Initial concentration of formaldehyde, 3 mg per 100 ml. 1) Solution of  $\text{H}_2\text{CO}$ ; 2) solution of  $\text{H}_2\text{CO}$  in the presence of  $4 \cdot 10^{-2}$  M glycine.

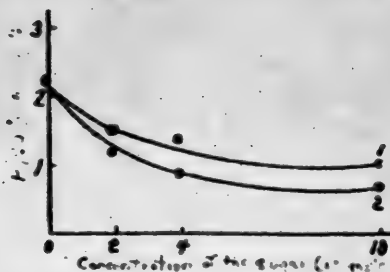


Fig. 5. Effect of ultrasound on the formation of  $\text{H}_2\text{CO}$  in methyl alcohol in the presence of sugars. Sonation time, 2 hours. 1) In the presence of glucose; 2) in the presence of lactose.

the alcohol not containing the amino acid.

Results of the action of ultrasound on the formation of formaldehyde in 0.1% solutions of methyl alcohol in the presence of glucose and lactose are given in Fig. 5. The curves show that the addition of sugars to solutions of methyl alcohol also causes a decrease in the formation of formaldehyde, which is greater with lactose than with glucose. The

amount of formaldehyde formed under these conditions was 0.75 mg per 100 ml, i.e., less than in the presence of each of these substances alone.

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The experimental material given in the present communication shows the complexity and the various forms of the chemical reactions occurring under the influence of ultrasound. This fact must be considered during examination of the problems of chemical and dispersive actions of ultrasonic vibrations.

## SUMMARY

1. The action of ultrasound on aqueous solutions of methyl, ethyl, n-propyl, and n-butyl alcohols was studied.

2. It was shown that formaldehyde, nitrous and nitric acids were formed upon the sonation of solutions of methyl alcohol.

3. The longer the carbon atom chain in the alcohol molecule, the more readily was the latter oxidized in the ultrasonic pole, and the more actively does it "protect" the nitrogen of air dissolved in the liquid from oxidation.

4. It was shown that the oxidation of alcohols by the action of ultrasound was hindered by the presence of aminoacids and sugars in the solutions of methyl alcohol.

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Received February 28, 1953.

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## THERMOCATALYTIC TRANSFORMATIONS OF HYDROCARBONS

### III. TRANSFORMATION OF DIPHENYLMETHANE

A. F. Dobryansky and P. N. Kolomytsev

Thermocatalytic transformations of diphenylmethane hydrocarbons up to now have been insufficiently studied, especially in the cases of low temperature transformations. For benzene homologs this transformation results finally in the transposition of a radical from one molecule to the other, whereby the benzene ring with the least degree of substitution is liberated. With anhydrous aluminum chloride diphenylethane is transformed in such a manner that benzene is cleaved and the residue, benzil, adds to another molecule of diphenylethane with the formation of diphenethylbenzene. The analogous action of anhydrous aluminum chloride and aluminosilicates, on the one hand, and the possibility of comparing diphenylmethane with diphenylethane, on the other, led to the expectation that diphenylmethane with an aluminosilicate catalyst would undergo similar transformations related to the equilibrium between the products formed, i.e., benzene and dibenzylbenzene.

Experiments on the catalytic transformation of diphenylmethane were conducted in two ways: with the distillation of the volatile products formed, and in an autoclave, in both cases with activated gumbrin as the catalyst. In the experiments conducted at the usual pressures in an iron still, and in experiments in an autoclave, qualitatively identical results were obtained: benzene was obtained in the distillate, and substitution products of diphenylmethane in the residue, mainly p-dibenzylbenzene; therefore the reaction indeed proceeds as in the case of aliphatic benzene homologs, according to the scheme:



### EXPERIMENTAL

Experiments in an autoclave. Diphenylmethane and the catalyst, gumbrin activated by hydrochloric acid, were taken in a quantitative ratio of 1:1. Only three experiments were conducted, differing in the length of heating (1 hour and 45 min., 5 hours, 10 hours). The temperature was 200° in all experiments. At the end of the reaction, the products obtained were distilled, with the more volatile being distilled first at temperatures lower than used during the experiment; the catalyst was then extracted with benzene, after the removal of which, the residue was added to the previously distilled part.

The first fraction had a b.p. 79.5-81°,  $d_4^{20}$  0.873. The yield of this fraction was about 95% of the more volatile products distilled from the autoclave, so that this part of the reaction products contained nothing in addition to benzene. The next fraction distilling at 81-300° contained almost exclusively unreacted diphenylmethane. It was isolated in the form of crystals with m.p. about 20° (pure diphenylmethane melts at 26°). A thick tarry mass was obtained in the residue from the distillation from which many crystals separated upon standing. The separation of these presented some difficulties, and for this reason, the residue above 300° was vacuum distilled at 12 mm, and a fraction boiling at 245-250° (calculation for normal pressure gave about 405°) was obtained. The fraction distilled in this manner, rapidly crystallized and had an m.p. 86°. The following was found upon elementary analysis: C 93.15%; H 6.85%; M 256, 261, 254. Calculated for  $C_{22}H_{18}$ : C 93.02%; H 6.98%; M 258. These results correspond to dibenzylbenzene which has m.p. 86°. Therefore, it was proven that the transformation of diphenylmethane proceeds according to the same scheme as for benzene homologs. The above method for the separation of the reaction mixture was also applied for the investigation of the products of the transformation of diphenylmethane at usual pressure.

Experiments at ordinary pressure. A series of experiments was conducted for the purpose of investigating the equilibrium between the starting and newly formed products of the reaction. The extent of the transformation was checked by the yields of benzene, since no other readily volatile products were obtained during the reaction.

The experiments were conducted in an iron still by heating to reflux at 120, 135, 150, and 170° in the liquid for long periods. After definite periods of time, the still was cooled, and a definite amount of the liquid products was removed with a pipette, and was investigated for benzene content by distillation to 90°. The distillate obtained was considered to be benzene, and its quantity calculated on the total amount of diphenylmethane used. Then the benzene along with the residue of its distillation, was returned to the still, and the heating was continued. In all, 24 experiments were conducted (see Table).

Yield of Benzene (in %) During the Transformation of Diphenylmethane at Various Temperatures and Heating Times

Experiment No.	Temperature	Heating time (in hours)	Yield of benzene (in %)	Experiment No.	Temperature	Heating time (in hours)	Yield of benzene (in %)
1	120°	2.5	0.49	13	150	5	9.03
2	120	5	1.40	14	150	10	9.20
3	120	10	2.32	15	150	15	9.30
4	120	15	2.39	16	170	0.5	6.80
5	135	1.25	3.62	17	170	1.25	9.0
6	135	2.5	5.60	18	170	2.5	10.5
7	135	5	6.10	19	170	5	11.3
8	135	10	6.30	20	170	10	11.6
9	135	15	6.40	21	170	15	11.5
10	150	0.5	2.90	22	200	1.75	20.0
11	150	1.25	6.50	23	200	5	21.7
12	150	2.5	8.06	24	200	10	21.8

The last three experiments in the above Table were conducted in an autoclave. Examination of the data in the Table shows that equilibrium is attained at the following yields of benzene: at 120°, after 10 hours with a yield of benzene of 2.3%; at 135°, after 5 hours with a yield of benzene of 11%, and at 200°, after approximately 2 hours with a yield of benzene of 21%. Actually, equilibrium was attained even at an earlier time, but the Table cannot be used to judge this time because the experiments were conducted with the removal of samples with rather long intermediate times. Calculated graphically: at 120°, about 10 hours, at 135°, about 4 hours, at 150°, about 3.5 hours, at 170°, about 3 hours, and at 200°, about 2.5 hours.

An attempt was also made to obtain diphenylmethane from benzene and dibenzylbenzene, i.e., to accomplish an equilibrium leading from the reaction products to the starting substances. Benzene and dibenzylbenzene in a ratio of 1:1 with an equal amount of activated clay was heated to reflux for 33 hours. The temperature of the mixture was initially equal to the boiling point of the mixture, i.e., 110°; after 33 hours, it increased to 116°, after which analysis of the mixture showed the presence of 7% of diphenylmethane in it. This experiment, however, cannot have any quantitative character, and an experiment in the autoclave, where it would have been possible to raise the temperature, would have been more conclusive.

The possibility of re-use of the activated gumbrin was checked in a series of experiments. A catalyst treated for a prolonged time at 135°, was used for the experiment. After washing it with benzene and drying at 250°, 100 g of such a catalyst and 100 g of diphenylmethane were heated for 2.5 hours at 170°; 10.4 g of benzene was obtained; this meant that the re-use of the catalyst was possible, and that the stopping of the reaction was caused by attainment of equilibrium, and not by poisoning of the catalyst.

#### SUMMARY

1. Diphenylmethane is very readily transformed into benzene and dibenzylbenzene in the presence of aluminosilicate catalyst even at 120°.
2. Methylbenzene was not formed at all during these transformations.
3. The transformation reaction has an equilibrium character, and diphenylmethane was formed by heating dibenzylbenzene with benzene.

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Received March 16, 1953.

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# INVESTIGATIONS OF CONJUGATED SYSTEMS

## I. SYNTHESIS AND PROPERTIES OF BROMOPRENE HOMOLOGS

E. A. Leporskaya and A. A. Petrov

Recently, because of the discovery of outstanding rubbergenic properties of dienic halogen derivatives, many investigations have been conducted on the synthesis of these substances by various methods [1]. The synthesis and properties of halogen derivatives of butadiene have been studied in the greatest detail. There is a considerable blank, however, in regard to the homologs of the latter. This is especially true for the bromine compounds.

We decided to prepare a series of normal homologs of bromoprene, because of a previous study of the peculiarities of reactions of dienic halogen derivatives with alkyl hypohalites [2, 3]. The corresponding chloroprene homologs had previously been reported in the literature [4]. They were obtained by the reaction of homologs of vinylacetylene with hydrogen chloride in the presence of  $\text{Cu}_2\text{Cl}_2$ . Four homologs of bromoprene were obtained by an analogous method, the action of hydrogen bromide on alkylvinylacetylene in the presence of  $\text{Cu}_2\text{Br}_2$ .

These substances are colorless liquids with ethereal odors. Their constants are given in Table 1.

TABLE 1

Substance	Boiling point (in °)	Pressure (in mm)	$d_4^{20}$	$n_D^{20}$	$M_R^D$	
					Found	Calculated
$\text{CH}_2=\text{CH}-\text{CBr}=\text{CH}_2$ [5] . . . .	42-43	165	1.3970	1.4988	27.94	27.50
$\text{CH}_2=\text{CH}-\text{CBr}=\text{CH}_2-\text{CH}_3$ . .	67.5-68.5	120	1.3308	1.5113	33.11	32.12
$\text{CH}_2=\text{CH}-\text{CBr}=\text{CH}-\text{C}_2\text{H}_5$ . .	86.5-87	120	1.2706	1.5070	37.84	36.74
$\text{CH}_2=\text{CH}-\text{CBr}=\text{CH}-\text{C}_3\text{H}_7$ . .	64-65	20	1.2210	1.5040	45.46	41.36
$\text{CH}_2=\text{CH}-\text{CBr}=\text{CH}-\text{C}_4\text{H}_9$ . .	83-83.5	20	1.1829	1.5008	47.11	45.97

It is apparent from the data in Table 1 that there is a regular increase in the boiling point, decrease in the density, and in refractive index. All of the substances possess an exaltation in the molecular refractivity. Bromoprene deviates somewhat from its series of homologs: it has a considerably smaller refractive index and shows a smaller exaltation in the molecular refractivity. This is explained by the so-called "central disruption" of conjugation. This central disruption is leveled by the effect of the strongly polarizing system of substituents in the bromine homologs. A similar relationship occurs in the series of chloroprene and its homologs [1, 3]. The structure of the bromoprene homologs obtained was established on the basis of the study of their properties.

- 1) All of the substances polymerize and tar upon storage.
- 2) They eliminate bromine very slowly upon heating with alcoholic KOH solution.
- 3) They participate readily in dienic synthesis upon heating with esters of fumaric and maleic acids, and give the corresponding esters of alkylbromocyclohexenedicarboxylic acids, wherein the latter substances, like the starting ones, possess stability to alkalis in relation to the bromine atom.
- 4) A very intense frequency for the double bond of  $1628\text{ cm}^{-1}$  was found in the Raman spectrum of ethylbromoprene. The frequency for the triple bond was absent.

The first two, and the fourth property of the substances obtained indicate the presence of a conjugated system of double bonds in their molecules. The third property indicates that the bromine atom is found at the double bond.

Therefore, the only acceptable formula of the six possible for the products of the addition of hydrogen bromide to homologs of vinylacetylene is  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{R}$ .

## EXPERIMENTAL

For the preparation of the bromoprene homologs, the authors initially applied a method used for the preparation of bromoprene from vinylacetylene. A mixture of the enynic hydrocarbon and a solution of  $\text{Cu}_2\text{Br}_2$  in concentrated hydrobromic acid was shaken 8-10 hours. The yield of the alkylbromoprene was 10-15% under these conditions.

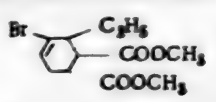
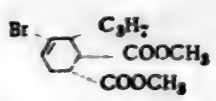
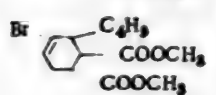
Better results were obtained by the addition of ammonium bromide or an amine hydrobromide to the reaction mixture. However, the yield of the alkylbromoprenes could not be raised above 30-35%. Thus, for example, 110 g of hexen-1-yne-2 was shaken for 10 hours with a solution of 110 g of  $\text{Cu}_2\text{Br}_2$  in 375 g of a solution of hydrogen bromide saturated at 0° (d 1.64) into which 9 g of methylamine was passed initially. The reaction products were separated from the aqueous layer, washed with water, dried with  $\text{CaCl}_2$ , and vacuum distilled. Results of distillation at 120 mm: 1) to 78°, 62.5 g (starting hydrocarbon), 2) 78-85°, 1.3 g, 3) 86-88°, 44.2 g, 4) 89-90°, 3.8 g, 5) residue, 13 g.

Table 2 gives the analytical results for the bromoprene homologs.

TABLE 2

Substance	Sample (in g)	Weight of AgBr (in g)	% Br	
			Found	Calculated
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$ .....	0.1168	0.1494	54.43	54.36
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{C}_2\text{H}_5$ .....	0.1282	0.1508	50.05	49.62
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{C}_3\text{H}_7$ .....	0.1194	0.1293	46.08	45.65
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{C}_4\text{H}_9$ .....	0.1160	0.1164	42.70	42.24

TABLE 3

Substance	Boiling point at 10 mm (in °)	$d_4^{20}$	$n_D^{20}$	MR <sub>D</sub>		
				Found	Calculated	
 $\text{C}_6\text{H}_5$ $\text{COOCH}_3$ $\text{COOCH}_3$	from the maleate	165-166	1.3796	1.5035	65.89	66.02
	from the fumarate	165-166	1.3693	1.5040	66.00	66.02
 $\text{C}_6\text{H}_7$ $\text{COOCH}_3$ $\text{COOCH}_3$	from the maleate	169-170	1.3308	1.5000	70.57	70.64
 $\text{C}_6\text{H}_9$ $\text{COOCH}_3$ $\text{COOCH}_3$	from the maleate	178.5-179.5	1.2996	1.4980	75.15	75.26
	from the fumarate	178-180	1.2926	1.4980	75.66	75.26

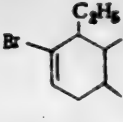
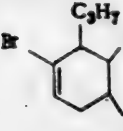
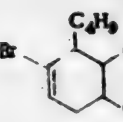
The condensation of the alkylbromoprenes with dimethyl fumarate and maleate was conducted in sealed tubes at 150° in toluene solution for 8 hours. These conditions were analogous to those generally used in the authors' laboratories during the study of the condensation of esters of unsaturated acids with dienic hydrocarbons.

A small amount of dimethyl fumarate was always obtained in addition to the condensation products, in reactions with the maleic ester. Evidently, under the conditions of the reaction, an isomerization of maleate to fumarate occurs, possibly, as a result of the catalytic effect of traces of hydrogen bromide separating from the alkyl bromoprene upon heating. For this reason, it is believed that the condensation products obtained from alkylbromoprenes and diethyl maleate were not pure cis isomers.

The dimethyl esters of the alkylbromocyclohexenecarboxylic acids, obtained as a result of this condensation, were viscous, colorless, almost odorless liquids. Table 3 gives the constants of several of the substances isolated.

Analytical results for these substances are given in Table 4.

TABLE 4

Substance	Sample (in g)	Weight of AgBr (in g)	Weight of AgI (in g)	% Br		% CH <sub>2</sub> O	
				found	calculated	found	calculated
 <chem>BrC1=CC(C(=O)OC)=CC(C1)C(=O)OC</chem>	from the maleate	0.1163	0.0724	—	26.49	26.19	—
	from the fumarate	0.1319	0.8826	—	26.65	26.19	—
		0.0835	—	0.1274	—	20.17	20.33
 <chem>BrC1=CC(C(=O)OC)=CC(C1)C(=O)OC</chem>	from the maleate	0.1300	0.0777	—	25.43	25.04	—
		0.0866	—	0.1300	—	19.84	19.44
 <chem>BrC1=CC(C(=O)OC)=CC(C1)C(=O)OC</chem>	from the maleate	0.1180	0.0679	—	24.91	23.98	—
		0.1584	—	0.2256	—	18.82	18.62
	from the fumarate	0.1032	0.0584	—	—	—	—
		0.0800	—	0.1120	—	18.50	18.62

1 g of ethylbromoprene was heated on the boiling water bath with a 10% KOH solution (double excess) in methanol for 1 hour. 0.0384 g or 7.7% of the bromine present in the sample went into solution. In an analogous experiment with butylbromoprene, 7.6% of bromine went into solution. The products of the condensation of bromoprene homologs with dimethylfumarate practically do not eliminate bromine under these conditions.

#### SUMMARY

1. A series of homologs of bromoprene was obtained by the action of hydrogen bromide in the presence of  $\text{Cu}_2\text{Br}_2$  upon vinyl acetylene homologs.
2. The condensation of these substances with dimethyl maleate and fumarate was investigated.

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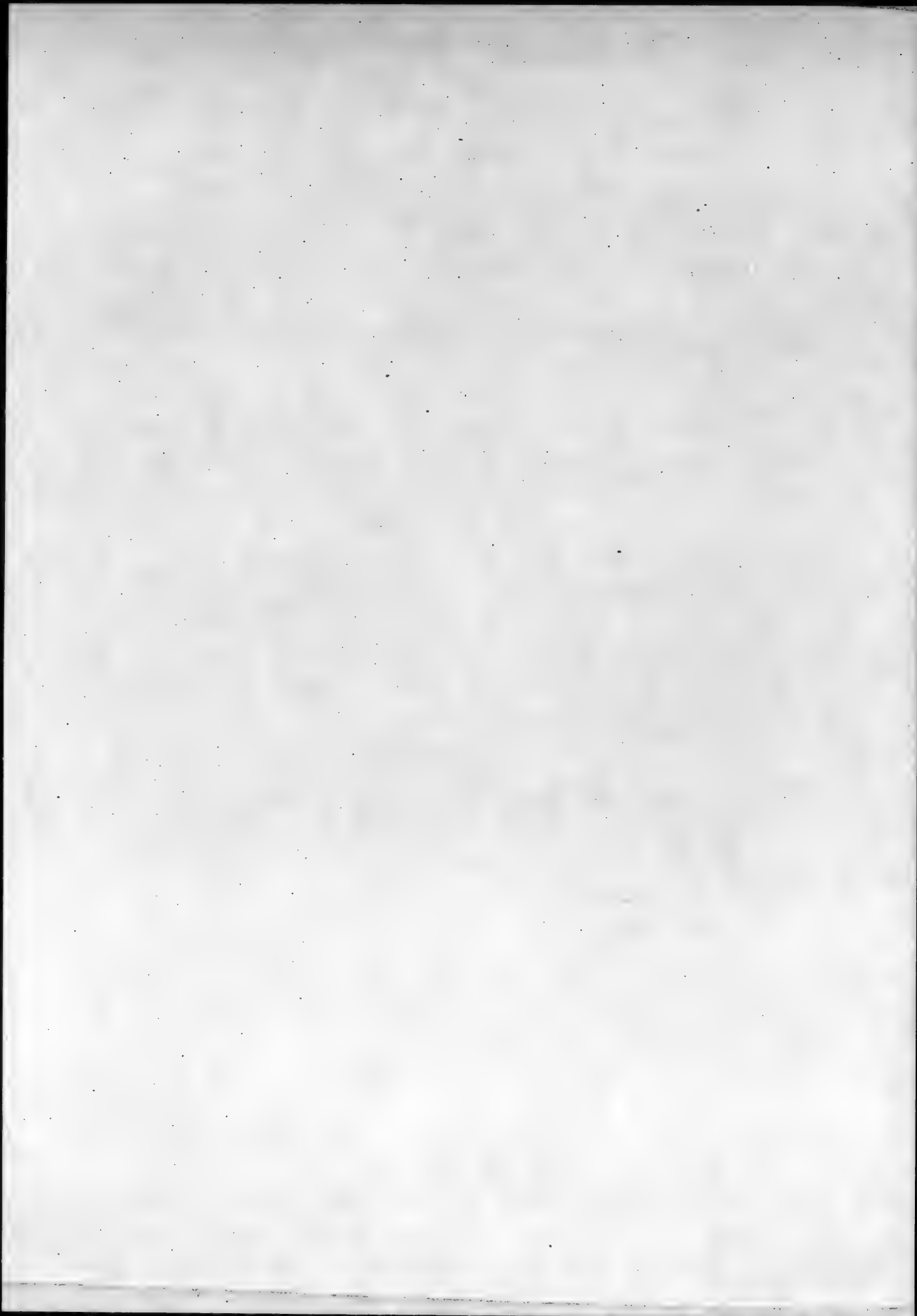
Received May 5, 1953.

Chemical Laboratory  
Leningrad Institute for  
Aviation Instrument Construction

\* See Consultants Bureau Translation, page 1557.

\*\* See Consultants Bureau Translation, page 1091.





## TERTIARY ACETYLENIC TRIOLS AND THEIR TRANSFORMATIONS

### IV. DEHYDRATION OF 2,3,6-TRIMETHYLHEPTYNE-4-TRIOL-2,3,6

V. I. Nikitin and A. Kh. Khamatov

Tertiary acetylenic glycerines, prepared by a method developed by one of the authors [1, 2], require a systematic study as a new, very interesting class of compounds. The molecule of such a glycerine, carrying three hydroxyl groups and an acetylenic bond, must possess the chemical properties of alcohols and glycols of the acetylenic series. On the other hand, certain peculiarities in the structure of these molecules must favor certain eccentricities in their chemical behavior, which are of theoretical and synthetic interest.

The relation of glycerines to dehydrating agents deserves attention.

It is widely known that  $\gamma$ -glycols, as well as acetylenic carbinols, lose water upon dehydration, with the formation of vinylacetylenic, or divinylacetylenic hydrocarbons.

Du Pont, who first used dilute sulfuric acid for the dehydration of the acetylenic  $\gamma$ -glycol, tetramethylneddiol [3], in addition to the main reaction product, diisopropenylacetylene, isolated dimethylisopropenylacetylenylcarbinol as an intermediate product resulting from the incomplete dehydration of the  $\gamma$ -glycol. Yu. S. Zalkind, E. D. Venus-Danilov and V. I. Ryabuseva [4] showed that the  $\gamma$ -glycol - asymmetrical dimethyldiphenylbutynediol - underwent a rearrangement into products isomeric to it under the action of an alcoholic solution of sulfuric acid. Depending upon the concentration of the acid, either a substituted tetrahydrofuranone or an  $\alpha$ -diketone with an open chain of carbon atoms - 2-methyl-5,5-diphenylpentandiol-3, 4 was formed. Glycols underwent a pinacol rearrangement with more or less ease under these conditions, which was first discovered by A. M. Butlerov [5] for saturated pinacols and was studied later in detail by Meerwein [6].

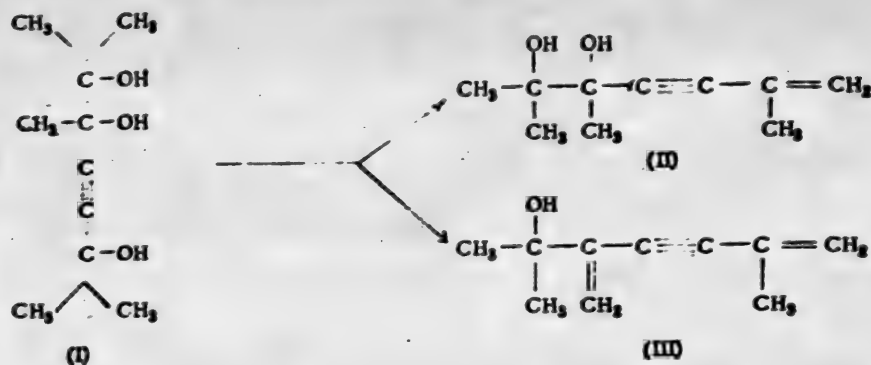
A. E. Favorsky and A. S. Onishchenko [7] treated the acetylenic  $\alpha$ -glycol, trimethylacetylenylethylene glycol, with concentrated sulfuric acid, and showed that the glycol mainly underwent a pinacol rearrangement to form an acetylenic ketone which was hydrated at once into the saturated diketone, 3,3-dimethylpentadione-2, 4.

E. D. Venus-Danilova and coworkers [8, 9, 10] showed that certain acetylenic  $\alpha$ -glycols underwent an acetylenyl-allenyl rearrangement under the action of sulfuric acid, as a result of which the unsaturated  $\gamma$ -keto alcohol was formed, which then cyclized into the substituted hydroxydihydrofuran. E. D. Venus-Danilova and L. A. Pavlova [11] also found that a pinacol rearrangement occurred with the acetylenic  $\alpha$ -glycol, methyl-diphenyltertiarybutylacetylenylethyleneglycol. By treating it with 30% sulfuric acid, they isolated an acetylenic ketone, 3,3-diphenyl-6, 6-dimethylheptyne-4-one-2, which formed in addition to the products of the acetylenyl-allenyl rearrangement. I. N. Nazarov and I. V. Torgov [12] obtained two products by the distillation of a vinylacetylenyl  $\alpha$ -glycol, trimethylvinylacetylenylethylene glycol, over potassium bisulfate: a dienynic carbinol, the product of the incomplete dehydration of the vinylacetylenyl  $\alpha$ -glycol, and a vinylacetylenyl ketone, a result of the pinacol rearrangement.

The results of the study of the action of dehydrating agents upon 2,3,6-trimethylheptyne-4-triol-2,3,6 (I) which is the simplest member of the tertiary acetylenic triols, is reported in the present communication.

Trimethylheptynetriol (I) was subjected to the dehydrating action of 20% sulfuric acid, potassium bisulfate, and p-toluene-sulfonic acid. The main product of the reaction, in all cases (from 40 to 62%) is the vinylacetylenyl  $\alpha$ -glycol, trimethylisopropenylacetylenylethylene glycol (2,3,6-trimethylheptyne-4-one-6-diol-2,3) (II) which was a glycerine-like liquid (b.p. 74-75° at 1.5 mm) obtained as a result of the loss of water from one of the hydroxyl groups of the acetylenyl triol. The dienynic carbinol, 2,6-dimethyl-3-methyleneheptyne-4-en-6-ol-2 (III) was always present in small amounts (about 4-5% of the triol reacted) in the dehydration products. (A mobile liquid, boiling at 73-74° at 6 mm), it is the product of the dehydration of the

heptynetriol with the participation of two of its hydroxyl groups:



The largest yield of the glycol (40% of the initial triol) was obtained with 20% acid upon dehydration with sulfuric acid. If 5-10% sulfuric acid was used for the reaction, a considerable part of the starting heptynetriol was recovered; a 30-50% acid caused a strong tarring.

The yield of the glycol (II) was 60-62% in the case of the dehydration of trimethylheptynetriol by vacuum distillation over potassium bisulfate, or *p*-toluenesulfonic acid.

Therefore, tertiary acetylenic glycerines do not undergo the isomeric transformations or pinacoline rearrangements under the conditions of the dehydration reaction, which could have been expected by analogy with  $\alpha$ -glycols.

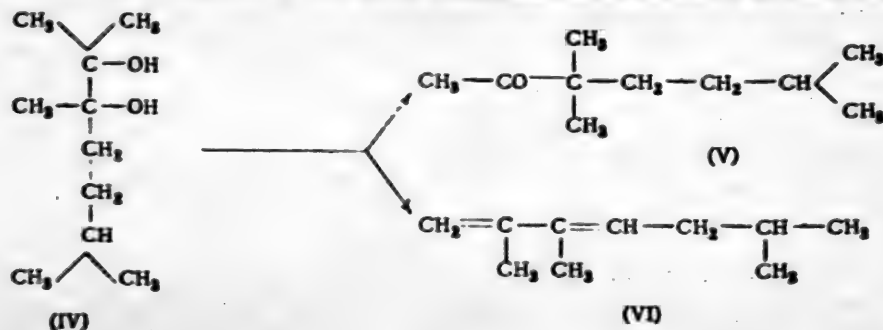
The structure of glycol (II) was proved by oxidation with a potassium permanganate solution; acetone, dimethylacetylcarbinol, formic acid, acetic acid, and oxalic acid were obtained. The structure of the dienynic alcohol (III), obtained with the glycol (II), was also proved by oxidation with potassium permanganate. Acetone, formic acid, acetic acid, and oxalic acid were obtained.

4 molecules of hydrogen were absorbed during the hydrogenation of the dienynic carbinol (III), which also confirmed its structure. The hydrogenation of trimethylisopropenylacetylene glycol (II), in the presence of a platinum catalyst in dry methanol solution, proceeded energetically at first, and then after the addition of 2 molecules of hydrogen, almost stopped. The product obtained distilled at 69-70° at 1.5 mm, and in all appearances, was an ethylenic  $\alpha$ -glycol. It was hydrogenated further with the absorption of 1 molecule more of hydrogen into the completely saturated glycol (IV).

The saturated  $\alpha$ -glycol, 2,3,6-trimethylheptanediol-2,3 (IV) (a crystalline product with m.p. 42-43°) obtained in this manner, underwent a pinacoline rearrangement by the action of sulfuric acid to give a ketone,

3,3,6-trimethylheptanone-2 (V) (a liquid with a pleasant odor with b.p. 65-67° at 11 mm), which readily formed a semicarbazone and 2,4-dinitrophenylhydrazone. The structure of ketone (V) as 3,3,6-trimethylheptanone-2 follows from the fact that a considerable amount of bromoform was obtained by oxidizing it with alkaline hypobromite.

In addition to the pinacoline rearrangement, the dehydration of glycol (IV) to the dienynic hydrocarbon, 2,3,6-trimethylheptadiene-1,3 also occurred partially; the latter could not be isolated in pure form. A fraction with b.p. 55-57° at 11 mm was obtained which contained ketone (V) as an impurity. It formed crystals with m.p. 134-135° with maleic anhydride; it could not be investigated further because of the small amount.



## EXPERIMENTAL

The initial 2,3,6-trimethylheptyne-4-triol-2,3,6 was prepared, as reported by one of the authors [1] by the condensation of dimethylacetylenylcarbinol with dimethylacetylenylcarbinol and had an m.p. 82-83°.

### I. Dehydration of 2,3,6-Tri-methylheptyne-4-triol-2,3,6.

**20% sulfuric acid.** A mixture of 50 g of 2,3,6-trimethylheptyne-4-triol-2,3,6 and 200 ml of 20% sulfuric acid was heated for 2 hours on a boiling water bath in a flask with a reflux condenser. The reaction product was extracted with ether, treated with a dilute sodium carbonate solution, dried with sodium sulfate, and then after the removal of the ether, vacuum distilled at 2 mm:

Fraction 1 with b.p. up to 76°, 2.4 g,  $n_D^{20}$  1.4960; fraction 2 with b.p. 76-77°, 18.0 g,  $n_D^{20}$  1.4888. Tarry residue, 20.6 g.

The fraction with b.p. 76-77° at 2 mm was, as it was shown, trimethylisopropenylacetylenylethylene glycol (II); yield 40% of theory based on the trimethylheptynetriol used for the reaction.

**Potassium bisulfate.** A mixture of 20 g of 2,3,6-trimethylheptyne-4-triol-2,3,6, 7 g of potassium bisulfate, and 0.1 g of pyrogallol was heated at 3-4 mm to 150-155° on a metal bath. 15.9 g of a substance distilled at 70-110°. A total of 140 g of trimethylheptynetriol was dehydrated in several experiments, and 99.3 g of crude product was obtained.

The crude reaction product was dissolved in ether, and dried with sodium sulfate. After several vacuum distillations, the following fractions were isolated:

Fraction 1 with b.p. 74-75° at 7 mm, 4.8 g,  $n_D^{20}$  1.5043; fraction 2 with b.p. 74-75° at 1.5 mm, 72.5 g,  $n_D^{20}$  1.4888; fraction 3 with b.p. 115-120° at 1.5 mm, 10.5 g (crystals).

The fraction with b.p. 115-120° at 1.5 mm was the starting 2,3,6-trimethylheptyne-4-triol-2,3,6. The yield of the fraction with b.p. 74-75° at 1.5 mm was 62% based on the heptynetriol consumed.

**p-Toluenesulfonic acid.** A mixture of 25 g of 2,3,6-trimethylheptyne-4-triol-2,3,6, 0.08 g of p-toluenesulfonic acid, and 0.1 g of pyrogallol was heated to 150-155° at 3-4 mm on a metal bath; 21.8 g of product was distilled at 70-105°. 25 g more of the trimethylheptynetriol was dehydrated under these conditions, and 21.9 g of product was distilled.

The products of both experiments were combined, dissolved in ether, dried with sodium sulfate, and distilled at 1.5 mm:

Fraction 1 with b.p. to 72°, 7.3 g,  $n_D^{20}$  1.4941; fraction 2 with b.p. 72-74°, 27.3 g,  $n_D^{20}$  1.4887; fraction 3 with b.p. 74° and above, 3.7 g; residue, 5.3 g.

Fraction 3 was the unreacted starting trimethylheptynetriol. The yield of the main fraction with b.p. 72-74° at 1.5 mm was 60%.

The similar fractions of all experiments were combined and redistilled in vacuum. After several redistillations, two fractions were obtained:

Fraction 1 with b.p. 73-74° at 6 mm,  $n_D^{20}$  1.5043; fraction 2 with b.p. 74-75° at 1.5 mm,  $n_D^{20}$  1.4888.

#### 1. Investigation of the Fraction with b.p. 73-74° at 6 mm.

$d_4^{20}$  0.9007,  $n_D^{20}$  1.5043. Found:  $MR_D$  49.34,  $C_{10}H_{14}O$ . Calculated:  $MP_D$  46.97.

0.1326 g substance: 0.3830 g  $CO_2$ ; 0.1146 g  $H_2O$ . 0.1440 g substance: 0.4178 g  $CO_2$ ; 0.1231 g  $H_2O$ .

Found %: C 78.77, 78.96; H 9.67, 9.56.  $C_{10}H_{14}O$ . Calculated %: C 80; H 9.33. 0.0992 g substance:

17 ml  $CH_4$  (27°, 688.8 mm). 0.0990 g substance: 16.8 ml  $CH_4$  (26.2° 688.8 mm). Found %: OH 10.75.

10.63;  $C_{10}H_{14}O$ . Calculated %: OH 11.3.

**Oxidation.** 200 ml of a 2% and then 700 ml of a 4% alkaline potassium permanganate solution (32 g of  $KMnO_4$  calculated for 7 active oxygen atoms for 1 molecule of the substance) were added dropwise with mechanical stirring over a 7-hour period to 6.5 g of the substance in 60 ml of water. After the addition of all of the  $KMnO_4$  solution, the manganese dioxide was filtered, and a distillate with the neutral substances was removed from the filtrate. The first drops of the distillate gave a 2,4-dinitrophenylhydrazone with m.p. 125-126° (from alcohol) with 2,4-dinitrophenylhydrazine. A mixed melting point with acetone 2,4-dinitrophenylhydrazone gave no depression. Other neutral substances were not detected.

The solution, after the removal of the neutral substances, was acidified with hydrochloric acid, and the volatile acids distilled with steam. 730 ml of a distillate was obtained which required 608.2 ml of 0.1 N NaOH containing 2.4 g of NaOH for neutralization. The presence of formic acid was established in the distillate by the calomel test, and that of acetic, by the cacodyl test.

The volatile acids were converted into silver salts. The mixture of silver salts of formic and acetic acids was boiled with water for the decomposition of silver formate; the precipitated silver was filtered through a hot funnel, and the silver acetate, which precipitated in the filtrate, was analyzed.

0.0962 g salt: 0.0619 g Ag. 0.0876 g salt: 0.0564 g Ag. Found %: Ag 64.40, 64.31.  $\text{CH}_3\text{COOAg}$ . Calculated %: Ag 64.65.

The solution remaining after the removal of the volatile acids, was extracted for 3 days with ether in an extractor. 1 g of oxalic acid with m.p. 101-102° was isolated from the ether extract. A mixed melting point with authentic oxalic acid gave no depression.

Therefore, the following were obtained as a result of the oxidation: acetone, formic acid, acetic acid, and oxalic acid.

Hydrogenation. 0.66 g of the substance, dissolved in 20 ml of dry methanol, was hydrogenated over platinum oxide (according to Adams) for 3 hours. 370 ml of hydrogen was absorbed at 20° and 694 mm. Calculated for 4 moles of hydrogen, 384 ml.

According to the results of the oxidation and the hydrogenation, the fraction boiling at 73-74° at 6 mm,  $n_D^{20}$  1.5043, was the dienynic carbinol, 2,6-dimethyl-3-methyleneheptyne-4-en-6-ol-2 (III).

The incomplete agreement of the results of the elementary analysis with calculated must be explained by the presence of some vinylacetylenic glycol (II) as an impurity.

## 2. Investigation of the Fraction with b.p. 74-75° at 1.5 mm.

$n_D^{20}$  1.4888,  $d_4^{20}$  0.9696. Found:  $M_R^{20}$  49.99.  $\text{C}_{10}\text{H}_{14}\text{O}_2$ . Calculated:  $M_R^{20}$  48.96.

4.925 mg substance: 12.882 mg  $\text{CO}_2$ ; 4.255 ml  $\text{H}_2\text{O}$ . 3.850 mg substance: 10.054 mg  $\text{CCl}_4$ ; 3.294 mg  $\text{H}_2\text{O}$ . Found %: C 71.38, 71.27; H 9.67, 9.57.  $\text{C}_{10}\text{H}_{14}\text{O}_2$ . Calculated %: C 71.43; H 9.52. 0.1120 g substance: 38.4 ml  $\text{CH}_4$  (34°, 685.1 mm). 0.1126 g substance: 38.6 ml  $\text{CH}_4$  (35°, 685.1 mm). Found %: OH 20.83, 20.89.  $\text{C}_{10}\text{H}_{14}\text{O}_2$ . Calculated %: OH 20.24.

Oxidation. 19.1 g of the substance in 100 ml of water was used and 2370 ml of a 3% potassium permanganate solution (71 g of  $\text{KMnO}_4$  calculated for 6 active oxygen atoms per mole of the substance isolated) was added dropwise with efficient stirring over a period of 7 hours.

The neutral substances were distilled with steam. The distillate with the neutral substances was concentrated by means of gradual distillation to 250 ml; acetone with b.p. 53-56°, 0.8 g, was obtained from the distillate with a rectifying column. It gave a semicarbazone with m.p. 187-188° with semicarbazide hydrochloride. A mixed melting point with authentic acetone semicarbazone gave no depression. The solution remaining after the distillation of the acetone was extracted for 3 days with ether in an extractor. The ether extract was dried with sodium sulfate, and distilled after the removal of the ether. 1.2 g of a substance distilled (b.p. 132-135°,  $n_D^{20}$  1.4120), which was dimethylacetylcannabinol which gave a semicarbazone melting at 160-161°. A mixed melting point with authentic dimethylacetylcannabinol semicarbazone did not give a depression.

The solution of salts, after the removal of the neutral substances, was acidified with sulfuric acid, and the volatile acids steam distilled. The volatile acids were extracted with ether from the distillate. After drying and the removal of the ether, three fractions were collected:

Fraction 1 with b.p. 90-96°, 1.3 g; fraction 2 with b.p. 96-110°, 0.6 g; fraction 3 with b.p. 110-115°, 3.1 g.

The fraction with b.p. 90-96° contained formic acid, which was qualitatively established by a calomel test.

The fraction with b.p. 110-115° was acetic acid, as was established by the formation of cacodyl oxide and the preparation of a silver salt.

0.0372 g salt: 0.0238 g Ag. 0.1185 g salt: 0.0758 g Ag. Found %: Ag 64.00, 64.23.  $\text{CH}_3\text{COOAg}$ . Calculated %: Ag 64.65.

3.5 g of oxalic acid with m.p. 101-102° was isolated from the non-volatile acids (mixed melting point).



Therefore, as a result of the oxidation of the fraction with b.p. 74-75° at 1.5 mm, the following were obtained: acetone, dimethylacetylcarbinol, and formic, acetic, and oxalic acids.

The results of the oxidation as well as other results of the investigation of the fraction with b.p. 74-75° at 1.5 mm, showed that the latter was a substituted vinylacetylenic  $\alpha$ -glycol trimethylisopropenylacetylenylethylene glycol (II).

Hydrogenation of trimethylisopropenylacetylenylethylene glycol. 6.65 g of the substance dissolved in 60 ml of dry methanol was hydrogenated over platinum oxide (according to Adams) at 12° and 698 mm. After the addition of 2 moles of hydrogen, a sharp decrease in the absorption of hydrogen occurred. 2250 ml of hydrogen was absorbed within 2 hours 20 min. (calculated for 2 moles, 2010 ml).

The experiment was repeated with 8.6 g of the substance in 60 ml of dry methanol.

After the removal of the methanol, the hydrogenation products of two experiments were combined and distilled at 69-70° at 1.5 mm. 14.5 g of a substance,  $n_D^{20}$  1.4610, was obtained, which was then hydrogenated in a solution of 50 ml of glacial acetic acid over platinum oxide. 1980 ml of hydrogen was absorbed at 15° and 698.3 mm (calculated 2180 ml). Therefore, a total of 3 moles of hydrogen were consumed by 1 mole of the substance.

The completely hydrogenated product was extracted with ether after the neutralization of the acetic acid, dried over potassium carbonate, and distilled at 1.5 mm:

Fraction 1 with b.p. to 72°, 0.8 g,  $n_D^{20}$  1.4570; fraction 2 with b.p. 72-76°, 12.5 g,  $n_D^{20}$  1.4593; residue, 0.8 g.

Upon redistillation of fraction 2, 11.5 g of a substance with b.p. 67-68° at 1 mm was obtained.

$n_D^{20}$  1.4522;  $d_4^{20}$  0.9101. Found:  $MR_D$  52.77.  $C_{10}H_{22}O_2$ . Calculated:  $MR_D$  52.63.

This fraction crystallized upon standing, and melted at 42-43° after recrystallization from benzene.

11.10 mg substance: 28.06 mg  $CO_2$ ; 12.25 mg  $H_2O$ . 9.07 mg substance: 22.95 mg  $CO_2$ ; 10.19 mg  $H_2O$ . Found %: C 68.99, 69.05; H 12.35, 12.56.  $C_{10}H_{22}O_2$ . Calculated %: C 68.90; H 12.73. 0.1294 g substance: 39.3 ml  $CH_4$  (20°, 589.9 mm). 0.1140 g substance: 34.2 ml  $CH_4$  (21.5°, 689.9 mm). Found %: OH 19.54, 19.21.  $C_{10}H_{22}O_2$ . Calculated %: OH 19.54.

Therefore, the fraction with b.p. 67-68° at 1 mm,  $n_D^{20}$  1.4522, was 2,3,6-trimethylheptandiol-2,3 (V).

## II. Dehydration of 2,3,6-trimethylheptandiol-2,3 (V).

A mixture of 17 g of the substance in 300 ml of 25% sulfuric acid was heated on the water bath for 4 hours at 80-90°. The reaction products were extracted with ether, neutralized with sodium carbonate, dried with sodium sulfate, and distilled at 11 mm to yield the two fractions:

Fraction 1 with b.p. 55-57°, 3.5 g,  $n_D^{20}$  1.4552; fraction 2 with b.p. 65-67°, 7.8 g,  $n_D^{20}$  1.4260.

### 1. Investigation of the Fraction with b.p. 55-57° at 11 mm

$d_4^{20}$  0.7923,  $n_D^{20}$  1.4552. Found:  $MR_D$  47.28.  $C_{10}H_{18}F_2$ . Calculated:  $MR_D$  47.43. 0.1602 g substance: 0.4664 g  $CO_2$ ; 0.1794 g  $H_2O$ . 0.1531 g substance: 0.4550 g  $CO_2$ ; 0.1725 g  $H_2O$ . Found %: C 79.45, 81.04; H 12.54, 12.80.  $C_{10}H_{18}$ . Calculated %: C 86.96; H 13.07.

Hydroxyl groups were not found by the method of Chugaev-Tserevnikov.

Condensation with maleic anhydride. 0.75 g of the substance with 0.7 g maleic anhydride in 6 ml of toluene was heated for 20 hours at 110-120° in a sealed tube. After removal of the solvent, the crystals which formed were filtered and washed with hot chloroform to remove the unreacted maleic anhydride. 0.2 g of crystals were obtained which were recrystallized from dichloroethane with the addition of several drops of methanol. The crystals melted at 134-135°, and were not subjected to further investigation because of the small amount.

On the basis of these results it can be concluded that the fraction with b.p. 55-57° at 11 mm was dienic hydrocarbon of structure (V) contaminated with a higher boiling ketonic fraction.

This conclusion was also confirmed by the fact that a small amount of semicarbazone was formed by treating the fraction with b.p. 55-57° at 11 mm with semicarbazide. However, the hydrocarbon purified by means of the semicarbazone could not be isolated because it completely polymerized into a light yellow glass-like mass upon an attempt to vacuum distill it.

## 2. Investigation of the Fraction with b.p. 65-67° at 11 mm.

$d_4^{20}$  0.8303;  $n_D^{20}$  1.4260. Found:  $MR_D$  48.12.  $C_{16}H_{24}O$ . Calculated:  $MR_D$  48.39.  
0.1770 g substance: 0.4950 g  $CO_2$ ; 0.2024 g  $H_2O$ . 0.1208 g substance: 0.3380 g  $CO_2$ ; 0.1402 g  $H_2O$ .  
Found %: C 76.26, 76.32; H 12.79, 12.98.  $C_{16}H_{24}O$ . Calculated %: C 76.84; H 12.85.

A semicarbazone with m.p. 132-133° (from 50% aqueous alcohol) was obtained in the form of needle-like crystals.

2.581 mg substance: 0.445 ml  $N_2$  (26°, 750 mm). 4.484 mg substance: 0.772 ml  $N_2$  (25°, 747 mm).  
Found %: N 19.42, 19.43.  $C_{11}H_{20}ON_2$ . Calculated %: N 19.71.

A 2,4-dinitrophenylhydrazone with m.p. 112-113° (from alcohol) was obtained in the form of gold-like scales.

4.663 mg substance: 0.667 ml  $N_2$  (21°, 743 mm). 4.383 mg substance: 0.640 ml  $N_2$  (23°, 745 mm).  
Found %: N 16.25, 16.51.  $C_{16}H_{24}O_4N_6$ . Calculated %: N 16.67.

Oxidation with alkaline hypobromite. 17.2 g of bromine was slowly added dropwise at -10° with mechanical stirring to a mixture of 5.6 g of the substance and 4.3 g of sodium hydroxide in 17 ml of water. After the addition of the bromine, the stirring was continued for 1.5 hours more. The mixture was then treated with thio-sulfate and the neutral substances extracted with ether. The ether extracts were dried over potassium carbonate, and after the removal of the ether, 8.3 g of a substance was obtained which was distilled at ordinary pressure. A fraction, 5.5 g, was collected at 146-148°; this fraction was bromoform according to the boiling point and the character of its odor.

The obtaining of bromoform by the oxidation of fraction with b.p. 65-67° at 11 mm, as well as other results of the investigation, indicated that it was the ketone, 3,3,6-trimethylheptanone-2 (V).

## SUMMARY

1. The dehydration reaction of 2,3,6-trimethylheptyne-4-triol-2,3,6 proceeded mainly with the elimination of only 1 molecule of water from the molecule of the alcohol to form a substituted vinyl-acetylenic  $\alpha$ -glycol.
2. The hydroxyl groups linked with two neighboring carbon atoms in the molecule of the tertiary triol possessed a great stability to the action of dehydrating agents.
3. Four new substances unreported in the literature were obtained: 2,3,6-trimethylheptyne-4-en-6-diol-2,3 (trimethylisopropenylacetylenylethylene glycol), 2,6-dimethyl-3-methyleneheptyne-4-en-6-ol-2,3,6-trimethylheptandiol-2,3, and 3,3,6-trimethylheptanone-2.
4. 2,3,6-Trimethylheptandiol-2,3 underwent a pinacolone rearrangement under the action of dehydrating agents to form the corresponding ketone, 3,3,6-trimethylheptanone-2.

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Received March 24, 1953.

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- \* See Consultants Bureau Translation, p. 1197.
- \*\* See Consultants Bureau Translation, p. 2309.
- \*\*\* See Consultants Bureau Translation, p. 197.
- \*\*\*\* See Consultants Bureau Translation, p. 87.

# 1,1-DIMETHYLCYCLOPROPANE

Ya. M. Slobodin, V. I. Gilgoryeva, and Ya. E. Shmulyakovsky

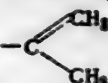
Cyclopropane hydrocarbons, according to their properties, occupy an intermediate position between the saturated and unsaturated hydrocarbons. They are capable of adding halogens and hydrogen halides. They are comparatively easily subjected to hydrogenation.

The addition of the hydrogen halide acids proceeds with great speed and in accordance with Markovnikov's rule, and leads to the cleavage of the bond in the three membered ring adjacent to the carbon atom which contains substituents [1, 2, 3].

The addition reaction of halogens with the cyclopropane hydrocarbons proceeds more complexly and leads most often to the formation of a mixture of products. The action of bromine on 1,1-dimethylcyclopropane was first studied by Gustavson [2]. He assigned the structure of 2,4-dibromo-2-methylbutane to the bromide formed on the basis of the fact that trimethylethylene was formed by the removal of bromine from it. This corresponded to the literature data [4] on the removal of bromine from 2,4-dibromo-2-methylbutane. However, later [5], it was shown that the hydrocarbon formed by the removal of bromine from 2,4-dibromo-2-methylbutane has erroneously been accepted as being trimethylethylene. Actually it is isopropylethylene.

In the present investigation the bromides formed by the action of bromine on 1,1-dimethylcyclopropane, as well as the hydrocarbons obtained by the removal of bromine from these dibromides, were studied.

Two lines with frequencies of  $1652\text{ cm}^{-1}$  and  $1680\text{ cm}^{-1}$  were found in the Raman spectrum of the hydrocarbon formed by the action of zinc dust upon the bromides obtained from 1,1-dimethylcyclopropane. The ratio of the intensities of these frequencies was 3:2. The frequency  $1680\text{ cm}^{-1}$  can be caused by the double bond of a trisubstituted ethylene. For a hydrocarbon of the composition  $\text{C}_5\text{H}_{10}$ , this can only be trimethylethylene. The frequency

$1652\text{ cm}^{-1}$  indicated the presence of a component in the hydrocarbon which contains the grouping 

For a hydrocarbon of the composition  $\text{C}_5\text{H}_{10}$ , only asymm. methylethylene can have this grouping. On the basis of visual evaluation it can be concluded that the obtained mixture of hydrocarbons contains about 40% of trimethylethylene and about 60% of asymm. methylethylene.

It could be expected that the bromides formed by the action of bromine upon 1,1-dimethylcyclopropane contained 40% of trimethylethylene bromide and 60% of asymm. methylethylene bromide, respectively. Raman spectra were made for verification. Table 1 gives the spectral data: the bromides obtained from 1,1-dimethylcyclopropane, and from a mixture consisting of 40% trimethylethylene bromide and 60% asymm. methylethylene bromide.

The practically complete identity of the spectra given in Table 1 proves the composition of the products of the bromination of 1,1-dimethylcyclopropane qualitatively and quantitatively.

The results obtained show that the reaction between bromine and dimethylcyclopropane proceeds quite complexly. It can be thought that in the first phase of the reaction bromine substitutes a hydrogen in the cyclopropane ring, as well as in the methyl group of the side chain. The hydrogen bromide formed adds at once to the cyclopropane ring, in accordance to Markovnikov's rule, and leads to the formation of both bromides.

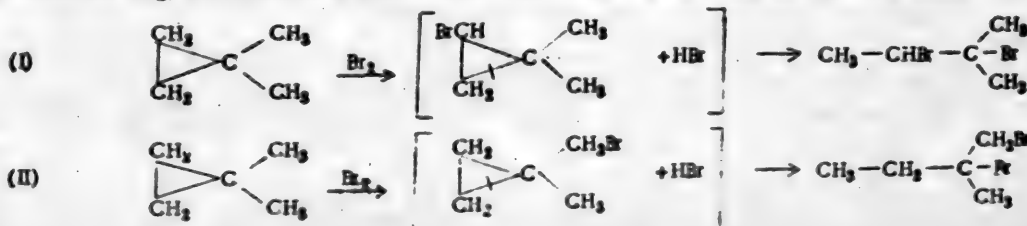


TABLE 1  
Raman Spectra\* of the Bromides  
(frequencies in  $\text{cm}^{-1}$ )

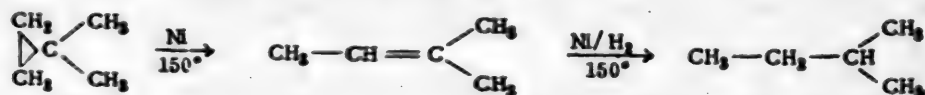
Bromides from 1,1-dimethylcyclopropane	40% trimethylethylene bromide, 60% asymm. methylethylene bromide	Bromides from 1,1-dimethylcyclopropane	40% trimethylethylene bromide, 60% asymm. methylethylene bromide	Bromides from 1,1-dimethylcyclopropane	40% trimethylethylene bromide, 60% asymm. methylethylene bromide
183(10)	184(8)	619(8)	618(8)	1026(2)	
294(5 w)	292(4 w)	634(10)	634(10)	1053(3)	1054(2)
322(2)	323(3)	655(1)	665(1)		1078(0.5)
387(2)	385(3 w)	682(1)		1100(4)	1105(5)
423(1)	418(0.5)	700(1)	703(1)	1167(3)	1167(4)
442(2)	437(0.5)	765(7)	765(8)	1208(2)	1210(2)
468(2)	466(2)	797(5)	797(7)	1224(5)	1227(6)
494(3)	493(3)	835(2)		1285(3)	1288(2)
517(2)	514(1)	863(4)	863(2 w)	1383(2)	1384(1 w)
543(2)	543(2)	880(2)			1431(4)
563(2)	560(2)	938(4)	936(2)	1445(4 w)	1453(3)

The problem of hydrogenation of cyclopropane hydrocarbons also is rather complex. Part of the known facts indicate that the hydrogen adds to the bond adjacent to the substituted carbon of the ring; another part of the known facts show that the addition of hydrogen also occurs at the bond opposite to the substituted carbon of the ring.

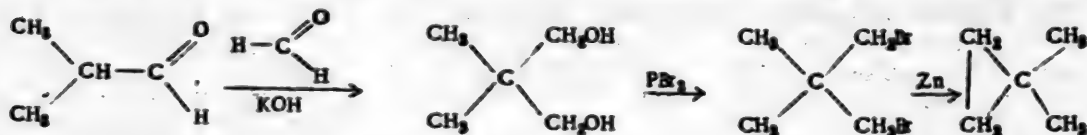
Thus Rozanov [3] obtained isopentane by hydrogenation of ethylcyclopropane. Isopropylcyclopropane, upon hydrogenation, was transformed into a mixture consisting mainly of 2,3-dimethylbutane [7], while isopropenylcyclopropane was converted into isohexane upon hydrogenation [8]. Kizhner [9] obtained a mixture of two hydrocarbons upon hydrogenation of 1-methyl-2-isopropylcyclopropane. 1,1,2-Trimethylcyclopropane formed a mixture of the three possible products upon hydrogenation [10].

The hydrogenation of 1,1-dimethylcyclopropane over a nickel catalyst, deposited on kieselguhr, at  $150^\circ$ , was studied in the present investigation. Isopentane without any noticeable contamination of the other hydrogenation product, neopentane, was obtained as a result. Therefore, the hydrogen added to the bond adjacent to the substituted carbon atom of the ring.

In order to determine the mechanism of hydrogenation, experiments with insufficient amounts of hydrogen were conducted. An intense line with a frequency of  $1630 \text{ cm}^{-1}$  appeared in the Raman spectra of the products obtained, which indicated the presence of considerable amounts of trimethylethylene in the mixture. In addition, all of the intense frequencies of 1,1-dimethylcyclopropane were retained in the spectra. This fact made it possible to suppose that the first act in these experiments on hydrogenation was the isomerization of 1,1-dimethylcyclopropane into trimethylethylene which was hydrogenated to isopentane:



The synthesis of the starting 1,1-dimethylcyclopropane was accomplished according to the scheme [13]:



\* The spectra were taken on the spectrograph ISP-51 with a camera of  $f = 270 \text{ mm}$ . The measurement of the lines was effected on the measuring microscope IZA-2, the calculation of the frequencies by Hartman's formula with the aid of a reference spectrum of Fe.

TABLE 2  
Raman Spectra of the Hydrocarbons  
frequencies in  $\text{cm}^{-1}$

Isopentane [11]	Products of the hydro- genation of 1,1-di- methylcyclopropane	Neopentane	Isopentane	Products of the hydro- genation of 1,1-di- methylcyclopropane	Neopentane
367(3)	361(2)	335(10)	1295(2)	1295(2)	
464(6)	460(5)	414(3)	1337(3 w)	1337(3 w)	
764(10)	764(10)	733(20)	1353(3 w)	1353(3 w)	1455(15)
796(8)	795(8)		1446(9 w)	1446(8 w)	2712(5)
909(5)	908(4 w)	925(15 w)	2721(2)	2721(1)	2745(3)
954(3)	951(2)		2735(1)		2794(3)
986(0)	986(3)		2854(12)	2854(8)	2864(7)
1014(3 w)	1011(3)		2875(31)	2871(20)	2892(5)
1035(5)	1035(4)		2909(13 h)	2910(10)	2911(10)
1147(4)	1146(4)		2935(17 h)	2935(12)	2937(3)
1177(4 s)	1179(4)		2965(18)	2961(12)	2955(3)
1267(1)	1265(1)	1252(20 w)			

## EXPERIMENTAL

### 2,2-Dimethylpropanediol-1,3

The diol was prepared by the condensation of isobutyraldehyde with formaldehyde in a solution of alcoholic alkali [13].

A solution of 35 g of KOH in 150 ml of alcohol was placed into a flask equipped with a stirrer and reflux condenser. A mixture of 30 ml of alcohol, 36 g of isobutyraldehyde, and 130 ml of 28% formaldehyde was added to the solution at 40° with efficient stirring over a 2 hour period. The flask was then heated for 18 hours at 80°. After the distillation of the alcohol, the residue in the flask was extracted for 5-6 hours with ether. The ether was removed. The diol was vacuum distilled.

B.p. 201-204° at 760 mm; m. p. 126°. Found %: C 57.73; H 11.68.  $\text{C}_5\text{H}_{12}\text{O}_2$ . Calculated %: C 57.69; H 11.63.

A total of 600 g of diol was prepared. The yield of the pure product was 50% of theory.

### 1,3-Dibromo-2,2-dimethylpropane.

0.25 mole of the diol was placed into a flask and 0.25 mole of  $\text{PBr}_3$  was added dropwise to it with cooling with ice water [14]. The temperature of the bath was then slowly raised to 100°. The water bath was replaced by an oil bath, and the mixture was kept for 18 hours at 150°. The contents of the flask were poured into cold water after cooling. The bromide was extracted with ether. The ether solution was washed with water and dried. After the removal of the ether, the bromide was distilled.

B.p. 182-183° at 743 mm and 14 mm;  $d_4^{20}$  1.6775;  $n_D^{20}$  1.5047;  $\text{MR}_D$  40.63. Found %: Br 68.60.  $\text{C}_5\text{H}_{10}\text{Br}_2$ . Calculated %: Br 69.60;  $\text{MR}_D$  41.05.

The yield of the bromide was 40% of theory. A total of 420 g of the substance was prepared.

### Raman Spectrum

167 (2), 212 (2), 274 (3), 330 (3), 372 (1), 404 (1), 443 (7), 594 (0.5), 644 (10), 663 (8), 703 (5), 758 (0.5), 863 (3), 904 (2), 916 (3), 959 (3 w), 1078 (2), 1122 (2), 1209 (0.5), 1265 (5 w), 1429 (4), 1459 (4).

### 1,1-Dimethylcyclopropane

1 Mole of zinc dust, 90 ml of alcohol, and 5 ml of water were placed into a flask with a reflux condenser and dropping funnel. The mixture was heated to boiling, and then 0.25 mole of 1,3-dibromo-2,2-dimethylpropane was slowly added. Water heated to 60° was circulated in the reflux condenser because of which the vapors of the



hydrocarbon formed passed through the condenser uncondensed, and entered a well-cooled coil. The hydrocarbon was washed with water, dried, and distilled over metallic sodium. Yield 90-95% of theory based on the dibromide.

B.p. 21°;  $d_4^{20}$  0.6618 (in a closed pycnometer);  $n_D^{25}$  1.3663;  $MR_D$  23.69.  $C_5H_{10}$ . Calculated:  $MR_D$  23.79. (The increment for the three membered ring was taken to be equal to 0.7)

#### Raman Spectrum

172 (1), 182 (1), 356 (3 w), 396 (2), 632 (1), 685 (8), 735 (0.5), 786 (1), 836 (6), 930 (10), 1058 (7), 1125 (2), 1183 (1), 1214 (2), 1230 (3), 1290 (1), 1321 (9), 1388 (0.5), 1432 (4), 1459 (4), 2737 (3), 2869 (8), 2895 (7), 2930 (6), 2956 (5), 2998 (20), 3061 (4 w).

The present spectrum is identical to that obtained by Cleveland [15].

#### Action of Bromine Upon 1,1-Dimethylcyclopropane

13 g of the hydrocarbon was placed into a flask with a reflux condenser, and 31.5 g of bromine was slowly added with cooling with ice water. The reaction proceeded violently. The bromide was separated, dried over calcium chloride, and distilled. A dibromide with b.p. 64.5° at 18 mm (82%) and a tribromide with b.p. 110-114° at 17 mm (18%) were isolated.

Properties of the dibromides:  $d_4^{20}$  1.6440;  $n_D^{20}$  1.5059;  $MR_D$  41.60. Found %: Br 69.07.  $C_5H_8Br_2$ . Calculated:  $MR_D$  41.05; % Br 69.60.

The Raman spectrum is given in Table 1.

Properties of the tribromide:  $d_4^{20}$  1.8761;  $n_D^{20}$  1.5366.

#### Removal of Bromine from the Dibromide

The bromine was removed in the usual manner by the action of zinc dust in alcoholic medium. Yield of the hydrocarbon: 73%.

B.p. 30.5-33°;  $d_4^{20}$  0.6530;  $n_D^{20}$  1.5366.

#### Raman Spectrum

265 (1), 348 (1), 396 (2), 439 (2), 526 (3 w), 593 (3 w), 611 (1), 769 (10), 924 (1), 1012 (1 w), 1189 (1), 1240 (1), 1332 (2), 1389 (3), 1428 (1), 1455 (3), 1594 (1), 1618 (2), 1652 (8), 1680 (6).

#### Hydrogenation of 1,1-Dimethylcyclopropane

The hydrogenation was effected in a flowing system. The catalyst was nickel deposited on kieselguhr. The experiment temperature was 150°. The catalyst was initially heated for 5 hours at 350° in a stream of hydrogen.

The hydrogen was passed through a graduated vessel containing the hydrocarbon. Due to the high volatility, the hydrocarbon vapor was entrained by the hydrogen, and the mixture entered into the reaction tube. The amount of hydrocarbon in the gaseous phase was regulated by cooling the vessel. The rate of passage of the hydrogen was measured with a flow meter. The rate of the introduction of the hydrocarbon was measured by means of its removal from the vessel. The volume velocity of the hydrogen was 150 liters per liter of catalyzate per hour. The products of the hydrogenation were collected in a trap cooled by dry ice. The hydrocarbon was dried and distilled. The Raman spectrum is given in Table 2.

B.p. 27.5-28°;  $d_4^{20}$  0.6185;  $n_D^{25}$  1.3537. (Literature data for isopentane [16]:  $d_4^{20}$  0.6197;  $n_D^{25}$  1.3539).

In separate experiments, hydrogenation was conducted with an insufficient amount of hydrogen. The reaction products boiled at 25-35°.

#### Raman Spectrum of the Hydrogenation Products

334 (1), 358 (3 w), 392 (2 w), 444 (1), 462 (1), 528 (3), 630 (1), 665 (1), 685 (8), 767 (8), 800 (2), 838 (7), 874 (1), 933 (10), 1061 (7), 1126 (0.5), 1232 (2), 1289 (1), 1322 (7), 1343 (2), 1386 (6), 1452 (7), 1680 (7), 2738 (0.5), 2865 (7), 2895 (1), 2923 (5), 2934 (5), 2965 (4), 2999 (8), 3064 (2).

Only isopentane was obtained as a reaction product upon a repeat of the hydrogenation.

## SUMMARY

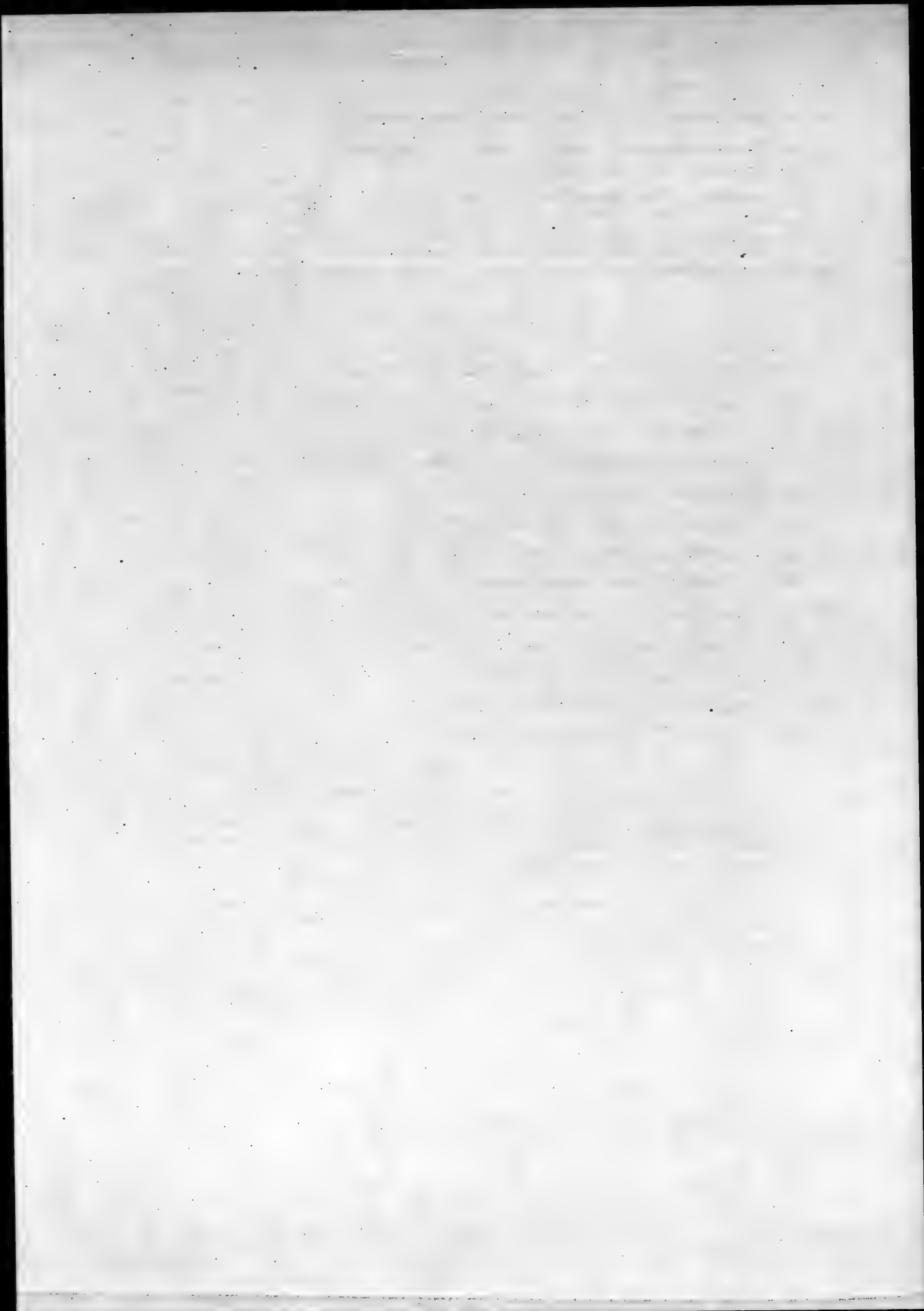
1. By the action of bromine upon 1,1-dimethylcyclopropane, a mixture of bromides containing 40% trimethylethylene bromide and 60% asymm. methylethylethylene bromide was formed.
2. The removal of bromine from the mixture of bromides obtained led to the formation of trimethylethylene and asymm. methylethylethylene in the same ratio.
3. Hydrogenation of 1,1-dimethylcyclopropane over nickel on kieselguhr at 150° led to the formation of isopentane.
4. By hydrogenation of 1,1-dimethylcyclopropane with an insufficient amount of hydrogen, the hydrocarbon mixture, in addition to unchanged 1,1-dimethylcyclopropane, contained trimethylethylene.

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Received March 14, 1953.

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Preparation of Commercial Liquid Paraffin.



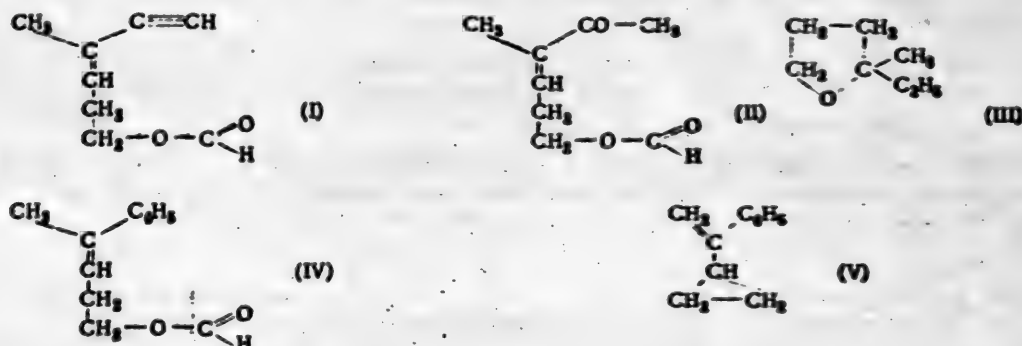
# MECHANISM OF THE TRANSFORMATION OF TERTIARY CYCLOPROPANE ALCOHOLS

## UNDER THE EFFECT OF MINERAL AND ORGANIC ACIDS

### I. REACTION OF DIMETHYLCYCLOPROPYLCARBINOL WITH FORMIC ACID

T. A. Favorskaya and N. V. Shcherbinskaya

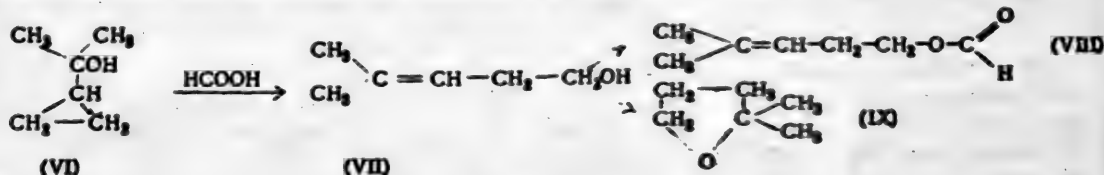
The reaction of formic acid with methylacetylenylcyclopropylcarbinol [1], methylethylcyclopropylcarbinol, and methylphenylcyclopropylcarbinol [2] was studied in previous investigations. In the first case, the formate of the primary enyne alcohol (I) and the product of its hydration, the ester of the ketoalcohol were obtained (II)



In the second case, the  $\gamma$ -oxide of methylethyltetramethylene, or 2,2-methylethyltetrahydrofuran (III) was obtained; in the third, the formate of the unsaturated alcohol (IV) and the product of the dehydration of the cyclic alcohol, asymm. phenylcyclopropylethylene (V). In all of these cases the concentration of formic acid was not lower than 80%, and the reaction was conducted with heating. Because of the sufficiently forcing reaction condition, no intermediate products were isolated in all three cases, and for this reason, all of the suggestions on the mechanism of the reactions were not final.

Milder conditions were used during the study of the reaction of dimethylcyclopropylcarbinol with formic acid: 50% instead of 80% formic acid was used; as a result a complex mixture of product was obtained from which five compounds were isolated whose structures were accurately determined, which made it possible to establish the general mechanism of the reaction of the alcohols studied with formic acid.

The first product of this reaction was the unsaturated primary alcohol, 2-methylpentene-2-ol-5 (VII), formed as a result of the intermolecular allylic rearrangement of the tertiary cyclic alcohol (VI) accompanied by the moving of the hydroxyl to the  $\beta$ -position, and the opening of the three membered ring



A similar type of allylic rearrangement was first discovered by A. E. Favorsky and I. A. Dyakonov [3] during a study of the action of phosphorous pentachloride upon acetyltrimethylene: the initially formed cyclic dichloride isomerizes into an ethylene derivative by means of the movement of one of the chlorine atoms into the  $\beta$ -position, and the opening of the ring.

The unsaturated alcohol obtained gave a small amount of a formate corresponding to it (VIII) under the conditions of the reaction; in addition, part of the alcohol was transformed into 2,2-dimethyltetrahydrofuran (IX). When formates (I) and (IV) were first obtained, their formation was explained in the same manner as the formation of the primary unsaturated chlorides by the action of hydrochloric acid upon dimethyl- and methylacetylenyl-cyclopropylcarbinol, i.e., it was assumed that first the substitution of a hydroxyl group of the cyclopropyl alcohol by a formate residue occurred, or by an atom of the halogen, then the movement of these functional groups into the  $\beta$ -position, and the opening of the ring.

However, the discovery of the unsaturated primary alcohol in the reaction products, required the abandonment of such an interpretation of the reaction mechanism because, first, primary alcohols esterify more readily than tertiary, and second, the formate residue does not rearrange as easily as a chlorine atom; upon boiling, the formate of the unsaturated alcohol obtained, the hydrolysis product was an unsaturated alcohol and not dimethylcyclopropylcarbinol; the shift of the formate residue to the  $\gamma$ -position and the formation of the starting cyclic alcohol did not occur, whereas unsaturated primary chlorides give the starting cyclic alcohols upon hydrolysis. In addition, upon heating alcohol (VII) with formic acid, part of it was actually converted into the ester corresponding to it.

The determination of the mechanism of formation of formate during the reaction of tertiary cyclic alcohol with formic acid made possible the correct explanation of the mechanism of Rupe's [4] reaction of dimethylacetylenylcarbinol with formic acid which resulted in the formation of dimethylacrolein. Rupe explained this reaction by the consecutive hydration and dehydration of the acetylenic alcohol.

When the acetylene-allene-dienic rearrangement of chlorides formed by the action of hydrochloric acid upon dimethylacetylenylcarbinol was first studied [5], it was suggested that the formation of dimethylacrolein during Rupe reactions occurred as a result of a similar rearrangement.

Now it is considered that this reaction can be explained more simply: under the influence of formic acid, a shift of the hydroxyl group of the acetylenic alcohol to the  $\beta$ -position occurs, with the formation of an allenic hydroxyl derivative, which then isomerizes into dimethylacrolein.

One of the main products of the reaction of dimethylcyclopropylcarbinol with formic acid was 2,2-dimethyltetrahydrofuran, which was obtained by N. D. Zelinsky [6] by the action of oxalic acid upon dimethylcyclopropylcarbinol. He explained its formation by means of an intermediate product, a saturated  $\gamma$ -glycol (X).

It was shown by the authors that the source of the formation of  $\gamma$ -oxide was the unsaturated primary alcohol (VII). This alcohol vacuum distills without decomposition; upon distillation at ordinary pressure and in the presence of even minute amounts of acids, it isomerizes into the tetrahydrofuran derivative (IX).

The question of the cyclization of various compounds into tetrahydrofuran derivatives was the subject of many investigations. In more recent investigations, the conversion of  $\gamma$ - and  $\delta$ -glycols into derivatives of tetrahydrofuran and pyran [7-14] by heating with sulfuric acid of various concentration was studied. The first investigators studying the formation of derivatives of tetrahydrofuran and pyran by the cyclization of the corresponding unsaturated alcohols in acidic media, considered that they occurred by means of an intermediately-formed glycol or halohydrin. Such a view was held by N. D. Zelinsky [6] as an explanation of the formation of dimethyltetrahydrofuran from dimethylcyclopropylcarbinol by the action of oxalic acid. Paul [15, 16] who obtained 2-methyltetrahydrofuran by the distillation of the  $\gamma$ -ethylenic alcohol, penten-4-ol in the presence of a small amount of concentrated sulfuric acid, suggested that the mechanism of this transformation consisted of the direct addition of the hydroxyl to the double bond, but later considered that the reaction proceeded cationotropically.

However, he believed that such a mechanism is possible only in the case of alcohols containing an end methylene group. In the rest of the cases, he considered that the reaction occurred according to Rupe's mechanism [14]. Colonge holds an analogous view on the mechanism of this reaction [17].

The authors believe that this interpretation of the mechanism of this reaction is incorrect. It was shown that 2-methylpenten-2-ol-5 converts into 2,2-dimethyltetrahydrofuran by distillation with traces of acids; the reaction, therefore, takes place in the complete absence of water, and for this reason it is rather impossible to accept a mechanism for the formation of dimethyltetrahydrofuran by means of an intermediate formation of a glycol. On this basis, it is considered that in all of the various cases, the formation of cyclic derivatives from alcohols occurs directly, and not by means of a complex course of hydration and dehydration.

I. N. Nazarov [18] believes that the cyclization reaction proceeds by means of the formation of carbonium and oxonium ions.



It is possible that in all of the above cases the reaction proceeds during cyclization by means of such a mechanism, or by means of the shifting of the hydrogen from the hydroxyl group to the 3-position.

2-Methylpentene-2-ol-5 was able to hydrate and give the glycol (X) under the conditions of heating with formic acid, whose formation was suggested by N. D. Zelinsky, and which was actually found by the authors among the reaction products.

The hydration of the double bond of the unsaturated alcohol seems more probable since the reaction conditions were sufficiently mild, and not one case of the addition of any reactant to the position of the rupture of the three-membered ring has been found. Even under more forcing conditions, during heating of methylphenylcyclopropylcarbinol with 80% formic acid, the hydrocarbon phenylcyclopropylethylene (V) was found among the reaction products, in which the trimethylene ring was stable under the conditions of the reaction and did not hydrate; it is opened under these conditions only by an isomeric transformation as a result of an unusual allylic rearrangement. Glycol (X) and the primary monoester corresponding to it were isolated, the products of the reaction of dimethylcyclopropylcarbinol with small amounts of formic acid.

In order to determine the properties of this glycol, it was synthesized from acetopropyl alcohol and ethyl magnesium bromide. Its constants corresponded sufficiently well with those of the glycol isolated from the reaction products and with the literature data [8]. It was found that if this glycol was heated with 50% formic acid to 60-70°, it was converted into the monoester; if it was heated with this acid to boiling then, in addition to the ester, derivatives of tetrahydrofuran were also formed. The glycol isolated was a primary tertiary  $\gamma$ -glycol; in view of the fact that tertiary alcohols esterify less readily, it could be thought that the monoester formed during the reaction with formic acid was primary, which indeed was proved by the fact that this ester gave a positive reaction for the tertiary hydroxyl [19]. The glycol was formed by the hydrolysis of this ester. The ester vacuum distills without decomposition; upon distillation at ordinary pressures, it eliminates formic acid.

The structure of the primary unsaturated alcohol (VII) was not determined, as its constants coincided with those given by Van Aerde [20]. The structure of its ester was proved by hydrolysis in alkaline medium, which resulted in the isolation of alcohol (VII); in addition, since the isomeric transformations were possible under these conditions of hydrolysis, the alcohol was also obtained by the action of an organo magnesium compound upon the ester. Acetone was obtained upon oxidation of the ester; acrylic acid was obtained in a mixture with large amounts of formic acid, from which it could not be purified. The structure of 2,2-dimethyltetrahydrofuran was proved by its oxidation with  $\text{KMnO}_4$  solution; the oxidation proceeded slowly but, nevertheless, went to completion at room temperature. The only product of the oxidation was the lactone of  $\gamma$ -hydroxycaproic acid, which was then converted to the silver salt.

Parallel with the reaction of dimethylcyclopropylcarbinol with formic acid, reaction of formic acid with another tertiary alcohol  $\text{C}_6\text{H}_{13}\text{O}$ , namely, dimethylallylcarbinol, was studied. As the authors, along with Sh. A. Fridman [21], showed, methylethylallylcarbinol isomerized, by the action of  $\text{H}_2\text{SO}_4$ , into the primary alcohol, 3-methylhexene-3-ol-6. If analogous transformation had occurred in this case, then 2-methylpentene-2-ol-5 should have been obtained, which then would have given 2,2-dimethyltetrahydrofuran.

However, this isomerization did not occur in experiments conducted under various conditions. If the reaction was conducted heating with acid diluted 1:1, or with concentrated acid at 0°, then dimethylallylcarbinol was recovered unchanged; only small amounts of dehydration products were formed. On heating dimethylallylcarbinol with concentrated  $\text{HCOOH}$ , the dehydration proceeded more completely, and condensation products were formed. A substance was isolated from the mixture of products, which must be accepted as the trimer of the hydrocarbon  $\text{C}_6\text{H}_{10}$  on the basis of analytical results. The product obtained did not decolorize a  $\text{KMnO}_4$  solution, and did not add bromine from a chloroform solution. Apparently, a product of cyclic structure was formed as a result of polymerization, which did not contain double bonds, or a side chain. The structure of the hydrocarbon was not investigated more fully.

## EXPERIMENTAL

### Synthesis of Dimethylcyclopropylcarbinol.

The starting acetyltrimethylene was obtained from acetopropyl alcohol. Acetopropyl alcohol was converted into the bromide by distillation with a two-fold quantity of hydrobromic acid with b.p. 118-124°. The alcohol was added through a dropping funnel to the boiling acid in small portions, corresponding to the distillation of the bromide. The bromide distilled was separated from the water and used directly in the reaction. The yield of the crude product was 75-80%. Powdered alkali, (KOH or NaOH), in a quantity slightly greater than the theoretical,

was added with efficient shaking and mixing to the bromide which had been placed into a round-bottom flask and left to stand overnight. On the following day, the contents of the flask were dissolved in water, and the acetyltrimethylene steam distilled, salted out with potassium carbonate, dried, and distilled. B.p. 109-112°. Yield, 75% based on the crude bromide.

Dimethylcyclopropylcarbinol was obtained from methyl magnesium bromide and acetyltrimethylene. The product obtained, with b.p. 118-125° (63-70%), very rapidly decolorized a  $\text{KMnO}_4$  solution. For this reason, it was oxidized with  $\text{KMnO}_4$  to remove the unsaturated impurities. The yield of the pure product was 54-55%.

B.p. 120-123°;  $d_4^{20}$  0.888;  $d_4^{25}$  0.9653;  $n_D^{20}$  1.4323;  $M_{rD}$  29.21.  $\text{C}_6\text{H}_{10}\text{O}$ . Calculated:  $M_{rD}$  29.79.

The constants obtained corresponded to the literature data [5].

#### Reaction of Dimethylcyclopropylcarbinol with Boiling Formic Acid.

150 g of dimethylcyclopropylcarbinol was heated to boiling for 1.5 hours with 300 ml of formic acid (dilute 1:1 pH 0.44, or ~55%). After neutralization of the unreacted acid with dry sodium carbonate, the reaction products were extracted with ether.

After drying and removal of the solvent, the residue was distilled at ordinary pressure and then in vacuum. The following fractions were isolated after several redistillations: 1) 90-92°-28.8 g (19.2%). 2) 108-112°-6.2 g (5%). 3) 119-125°-4.0 g (5%). 4) 152-155°-35.5 g 5) 97.5-98.5° at 7 mm-18.9 g (8.6%). 6) 117-118° at 13 mm-5.5 g (3%).

In addition, intermediate fractions were obtained. Fraction 3, 119-125°, was the starting dimethylcyclopropylcarbinol.

Investigation of the fraction with b.p. 90-92°;  $d_4^{20}$  0.8477;  $n_D^{20}$  1.4901;  $M_{rD}$  29.18  $\text{C}_6\text{H}_{10}\text{O}$ . Calculated  $M_{rD}$  29.35.

0.1207 g substance: 0.3005 g  $\text{CO}_2$ ; 0.1141 g  $\text{H}_2\text{O}$ . Found %: C 71.82; H 11.82.  $\text{C}_6\text{H}_{10}\text{O}$ . Calculated %: C 72.9; H 12.0.

The substance slowly decolorized a  $\text{KMnO}_4$  solution and did not give reactions for hydroxyl or carbonyl groups which meant that it must be 2,2-dimethyltetrahydrofuran.

Oxidation. 5 g of the substance was oxidized for 2 days. The  $\text{MnO}_2$  residue was filtered and washed with hot water, the filtrate was evaporated to a small volume, and acidified with sulfuric acid, whereupon oil droplets floated on the surface. The oxidation products were extracted with ether. After drying with  $\text{Na}_2\text{SO}_4$  and removal of the solvent, a substance with b.p. 203-204°, the lactone of  $\gamma$ -hydroxyisocaproic acid, was obtained.

For the determination of the neutralization equivalent, the lactone was boiled with alkali, and the excess of the latter was titrated with hydrochloric acid.

0.1788 g substance: 42 ml  $\text{NaOH}$  (T 0.7456); 14.4 ml  $\text{HCl}$  (T 1.083). Found: E 113.7.  $\text{C}_6\text{H}_{10}\text{O}_2$ . Calc'd: E 114.0.

For the preparation of the silver salt of  $\gamma$ -hydroxyisocaproic acid, the lactone was dissolved in ammonia with heating on the water bath. The excess ammonia was removed by evaporation. A concentrated solution of  $\text{AgNO}_3$  was added to the solution of the ammonium salt obtained. The precipitated silver salt was filtered, washed with water, and dried in a desiccator.

0.1133 g substance: 0.0511 g Ag. Found %: Ag 45.10.  $\text{C}_6\text{H}_{10}\text{O}_2\text{Ag}$ . Calculated %: Ag 45.19

Investigation of the fraction with b.p. 108-112°. The substance gave a voluminous precipitate with 2,4-dinitrophenylhydrazine; the 2,4-dinitrophenylhydrazone melted at 145-146°; a mixed melting point with authentic acetyltrimethylene gave no depression. The dimethylcyclopropylcarbinol, used for the reaction with formic acid, was initially tested for acetyltrimethylene by means of 2,4-dinitrophenylhydrazine, and gave no precipitate with it. In order to conclusively determine whether or not acetyltrimethylene was present in the dimethylcyclopropylcarbinol, ultraviolet absorption spectra of both of these substances were made. For acetyltrimethylene, the character of the absorption curve coincided with that reported in the literature. A maximum at 270 m $\mu$  was found in the absorption spectrum of the alcohol, which indicated the presence of a carbonyl group in the compound. Therefore, acetyltrimethylene was present in the starting dimethylcyclopropylcarbinol. It could be isolated by distillation when the concentration of the alcohol decreased as a result of the reaction with formic acid. Therefore, acetyltrimethylene with 108-112° which was isolated, was not a product of the reaction between dimethylcyclopropylcarbinol and formic acid.

Investigation of the fraction with b.p. 152-155°. As shown by the investigation, this fraction was not an individual substance but a mixture of two products with close boiling points: the primary alcohol, 2-methylpentene-2-ol-5 and its formate. The constants of the fraction with b.p. 152-155°, isolated in several experiments, differed from each other, and apparently depended on the ratio of the components present.

$d_4^{20}$  0.9028, 0.9105, 0.9092;  $n_D^{20}$  1.4364, 1.4340, 1.4340. On conversion to  $C_7H_{14}O_2$ . Found:  $MR_D$  37.09, 36.60, 36.66. On conversion to  $C_8H_{16}O$ . Found:  $MR_D$  28.97, 28.61, 28.63,  $C_7H_{14}O_2F$ . Calculated:  $MR_D$  35.91,  $C_8H_{16}OF$ . Calculated:  $MR_D$  31.09.

A determination of the number of hydroxyl groups gave results which indicated the presence of 30-35% of the alcohol in the mixture. In order to show the presence of the ester in the mixture, the fraction 152-155° was subjected to hydrolysis.

20 g of the substance was heated with stirring with a two-fold quantity of 10%  $K_2CO_3$  solution for 8-10 hours. After extraction with ether, drying, removal of the solvent, and distillation, a fraction with b.p. 156-157° was obtained in a yield of about 80%. Its constants:  $d_4^{20}$  0.8556;  $n_D^{20}$  1.4464;  $MR_D$  31.20,  $C_8H_{16}OF$ . Calculated:  $MR_D$  31.09. Literature data for 2-methylpentene-2-ol-5: b.p. 157°;  $d_4^{20}$  0.8577, 0.8549;  $n_D^{20}$  1.4456, 1.4454.

0.0913 g substance: 0.2408 g  $CO_2$ ; 0.0972 g  $H_2O$ . 0.1387 g substance: 33.0 ml  $CH_4$  (13.5°, 761 mm). Found %: C 71.93, H 11.91. OH number 0.997.  $C_8H_{16}OF$ . Calculated %: C 72.0; H 12.0. OH number 1.

Therefore, only one product known in the literature, 2-methylpentene-2-ol-5, was obtained as a result of the hydrolysis of the fraction with b.p. 152-155°.

The aqueous solution remaining after the extraction of the alcohol was acidified with sulfuric acid. The volatile acids were steam distilled. A qualitative test with a mercuric chloride solution showed the presence of formic acid. The distilled solution of the volatile acids was titrated with NaOH; the amount of acid titrated showed that the fraction with b.p. 152-155° contained about 65% of the formate.

Investigation of the fraction with b.p. 97.5-98.5° at 7 mm. Upon attempting to distill the product at ordinary pressure, the formation of a noticeable amount of formic acid was noticed, whose presence was established by a qualitative reaction with mercuric chloride. The analytical results obtained showed that the fraction with b.p. 97.5-98.5° at 7 mm had the formula  $C_7H_{14}O_2$  and was the monoester of  $\alpha, \alpha$ -dimethyltetramethylene glycol and formic acid.

$d_4^{20}$  1.0123;  $d_4^{25}$  1.0256;  $n_D^{20}$  1.4395;  $MR_D$  37.97,  $C_7H_{14}O_2$ . Calculated:  $MR_D$  37.71. 0.1263 g substance: 0.2652 g  $CO_2$ ; 0.1083 g  $H_2O$ . 0.865 g substance: 14.4 ml  $CH_4$  (16.5°, 757 mm). 0.1083 g substance: 15.09 g benzene:  $\Delta t$  0.25°. Found %: C 57.34; H 9.67; OH number 1.001; M 141.  $C_7H_{14}O_2$ . Calculated %: C 57.51; H 9.65; OH number 1. M 142.

5 g of the fraction with b.p. 97.5-98.5° at 7 mm was hydrolyzed by heating and stirring with a two-fold quantity of 10% potassium carbonate solution for 1 day. After extraction with ether, drying, and removal of the solvent, the residue was vacuum distilled. One product with b.p. 112-113° at 12 mm was obtained.

$d_4^{20}$  0.9789;  $n_D^{20}$  1.4560;  $MR_D$  32.30,  $C_8H_{16}O_2$ . Calculated:  $MR_D$  32.65. 0.0939 g substance: 38.5 ml  $CH_4$  (16°, 757.8 mm). OH number 1.99,  $C_8H_{16}O_2$ . Calculated: OH number 2.

The constants of the substance obtained coincided with those of dimethyltetramethylene glycol synthesized by the authors.

The aqueous layer after the extraction of the glycol was acidified with sulfuric acid, and the volatile acids were steam distilled. Formic acid was detected in the distillate. In order to establish the position of the hydroxyl group in the ester, the qualitative Denigés [19] reaction was tried, and a voluminous yellow precipitate with mercuric oxide and sulfuric acid, characteristic for tertiary alcoholic groups, was obtained.

Investigation of the fraction with b.p. 117-118° at 13 mm.

$d_4^{20}$  0.9786;  $n_D^{20}$  1.4557;  $MR_D$  32.76,  $C_8H_{16}O_2$ . Calculated:  $MR_D$  32.96. 0.0893 g substance: 0.2008 g  $CO_2$ ; 0.0920 g  $H_2O$ . 0.0936 g substance: 36.9 ml  $CH_4$  (13.5°, 752 mm). Found %: C 61.32; H 11.52; OH number 1.93,  $C_8H_{16}O_2$ . Calculated %: C 61.01; H 11.86; OH number 2.

The substance obtained corresponds to  $\alpha, \alpha$ -dimethyltetramethylene glycol [8].

#### Reaction of $\alpha, \alpha$ -Dimethyltetramethyleneglycol with Formic Acid.

The glycol was prepared from methyl magnesium bromide and acetopropyl alcohol with a yield of about 40%.  $d_4^{20}$  0.9817;  $d_4^{25}$  0.9858;  $n_D^{20}$  1.4560;  $MR_D$  32.67.

**Experiment I.** 10 g of the glycol and 13 ml of formic acid, diluted 1:1, were heated to boiling for 1 hour, then the acid was neutralized with dry sodium carbonate, and the reaction products were extracted with ether. After drying and removal of the ether, the residue was distilled resulting in the isolation of: 2.4 g (28%) of a substance with b.p. 90-93° (2,2-dimethyltetrahydrofuran); 2 g of a fraction with b.p. 103-106° at 13 mm (16%) corresponding to the slightly impure monoester of the glycol, and 2.1 g of a fraction with b.p. 106-120° at 13 mm, a mixture of the ester and the starting glycol.

**Experiment II.** The glycol and the acid were heated on the water bath to 60-70° for 3 hours. The pure monoester of the glycol with b.p. 97-98° at 7 mm, 11.1 g (30%), a mixture of the glycol and ester with b.p. 98-112° at 7 mm, 8.5 g, and the starting glycol with b.p. 112-114° at 7 mm, 4.0 g (12%) were obtained.

Therefore, at 60-70° the formation of the oxide from the glycol does not occur; only the esterification of the glycol occurs.

#### Reaction of 2-Methylpentene-2-ol-5 and Its Ester with Formic Acid.

20.1 g of the mixture of the alcohol and ester was heated to boiling for 2.5 hours with 22 ml of HCOOH, diluted 1:1 (pH 0.44). After neutralization of the acid with dry sodium carbonate, the reaction products were extracted with ether. After drying, removal of the solvent, and distillation, the following fractions were obtained: 1) 90-93°—9.55 g (47.5%), 2) 93-152°—0.5 g, 3) 152-153°—0.5 g (starting product).

The constants of the substance with b.p. 90-93° coincided with those obtained for 2,2-dimethyltetrahydrofuran.

#### Reaction of Dimethylcyclopropylcarbinol with Formic Acid at 60-70°.

37 g of the alcohol was heated with 80 ml of formic acid (pH 0.44) for 1.5 hours at 60-70°. After usual processing of the reaction products and distillation, at first in vacuum and then at ordinary pressure, a mixture of the unsaturated alcohol and its formate with b.p. 152-155°, 20.1 g (54%) was isolated as the main product. In addition, small amounts of acetyltrimethylene (0.8 g) and the starting alcohol (0.5 g) were also isolated. No tetrahydrofuran derivatives were formed at these reaction temperatures.

#### Reaction of Dimethylallylcarbinol with Formic Acid.

Dimethylallylcarbinol was obtained according to R. Ya. Levina's method [22] from allyl chloride, magnesium, and acetone. 54 g of the alcohol with b.p. 116-118° (yield 54%) was obtained.

**Experiment I.** 12 g of the alcohol was boiled for 1.5 hours with HCOOH (1:1) (pH 0.44). As a result, 51% of the alcohol (6.1 g) was recovered; in addition 1.9 g of a fraction with b.p. 48-115° was obtained, from which a fraction with b.p. 70-82° was isolated, corresponding to a mixture of hydrocarbons obtained by the dehydration of dimethylallylcarbinol [21].

**Experiment II.** 40 g of dimethylallylcarbinol was stirred for 6 hours with concentrated HCOOH at 0°. As a result, unchanged dimethylallylcarbinol was recovered and about 1 g of hydrocarbons with b.p. 70-82° was isolated.

**Experiment III.** 44 g of the alcohol was boiled for 1.5 hours with concentrated HCOOH. The acid was neutralized with dry sodium carbonate. After extraction with ether, and distillation in vacuum, a substance with b.p. 142-143° at 12 mm, 87.3 g quantity, was obtained as the main product. The product did not decolorize a KMnO<sub>4</sub> solution, and the separation of HBr occurred upon the action of a bromine solution in chloroform. The results of elementary analysis showed that the substance was a hydrocarbon whose molecular weight corresponded to a trimer.

$d_4^{20}$  0.8659;  $n_D^{20}$  1.4905;  $M_{rD}$  81.92.  $C_{23}H_{36}$ . Calculated:  $M_{rD}$  81.01  
0.1071 g substance: 0.3421 g CO<sub>2</sub>; 0.1198 g H<sub>2</sub>O. 0.1515 g substance: 12.05 g benzene:  $\Delta t$  0.25°  
Found %: C 87.11; H 12.51; M 248.0.  $C_{12}H_{20}$ . Calculated %: C 87.80; H 12.20; M 246.

#### SUMMARY

1. The reaction of dimethylcyclopropylcarbinol with formic acid was studied
2. A mechanism for this reaction is given.
3. It was shown that, initially, the isomerization of dimethylcyclopropylcarbinol into the unsaturated primary alcohol, 2-methylpentene-2-ol-5, occurred by means of the shift of the hydroxyl to the B-position and the opening of the three-membered ring.
4. It was shown that the unsaturated alcohol partly formed the formate, and was partly isomerized to 2,2-dimethyltetrahydrofuran.



5. In addition to the above products, 2,2-dimethyltetramethylene glycol and the half ester of the glycol and formic acid were also isolated from the reaction products.

6. 2-Methylpentene-2-ol-5 was obtained upon hydrolysis of the ester of the unsaturated alcohol. The cyclic alcohol did not form.

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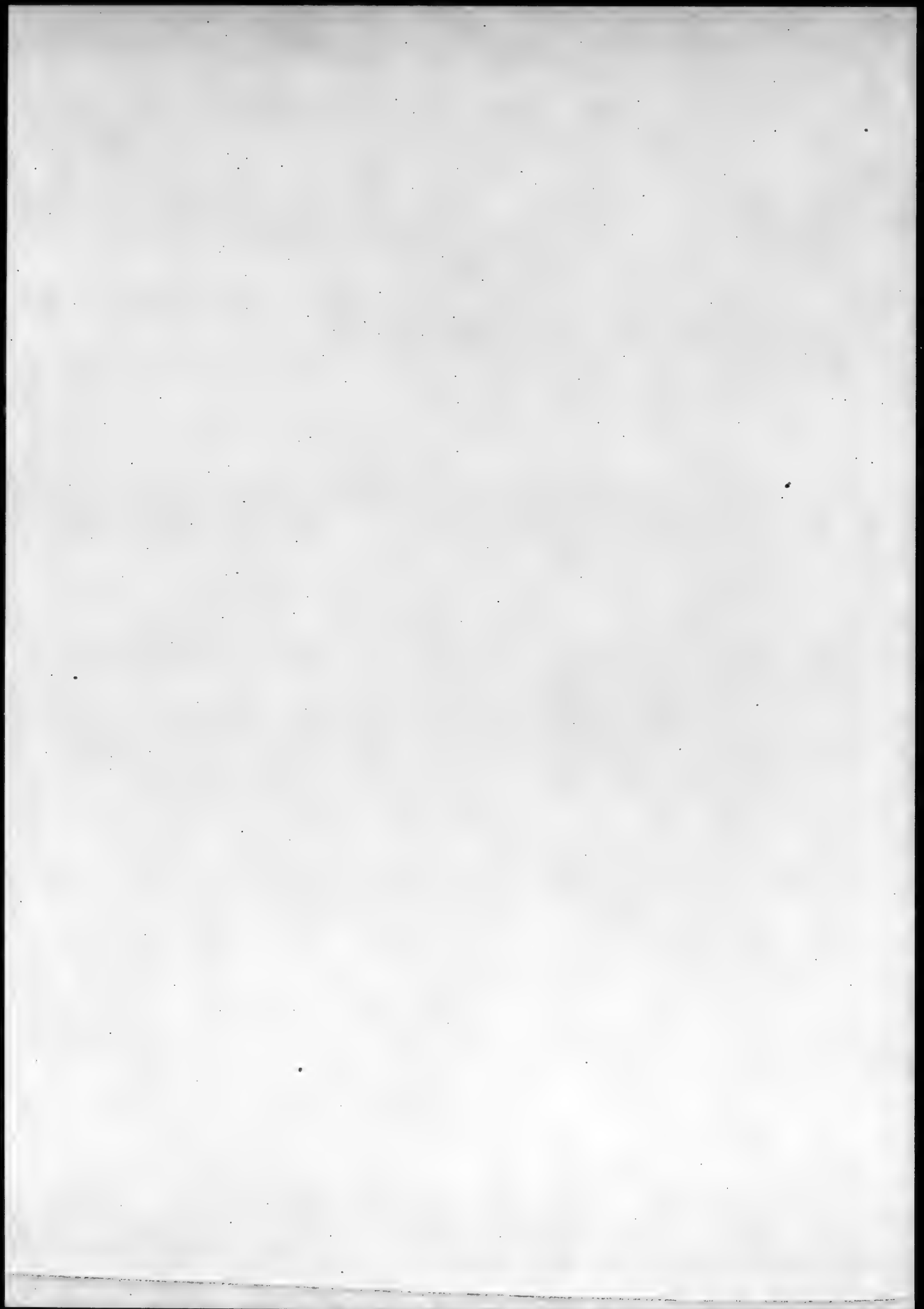
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Received May 4, 1953.

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Awarded the Order of Lenin.  
The A. E. Favorsky Laboratory.

• See Consultants Bureau English translation, page 891.  
•• See Consultants Bureau English translation, page 437.





# TRANSFORMATIONS OF ACETYLENIC ALCOHOLS CONTAINING POLYMETHYLENE RINGS

## II. 1-PHENYLACETYLENYLCYCLOHEXANOL-1

E. D. Venus-Danilova, M. V. Gorelik, and T. A. Nikolaeva

Recently one of the authors together with M. V. Gorelik [1] showed that 1-phenylacetylenylcyclopentanol-1 was transformed into the isomeric ethylenic ketone, cyclopentylideneacetophenone, in the presence of mercuric sulfate in acidic medium.

In order to determine to what extent an analogous reaction would occur for other tertiary polymethylene alcohols with acetylenic radicals, the behavior of 1-phenylacetylenylcyclohexanol-1 in an acidic solution of mercuric sulfate under the above conditions was studied.

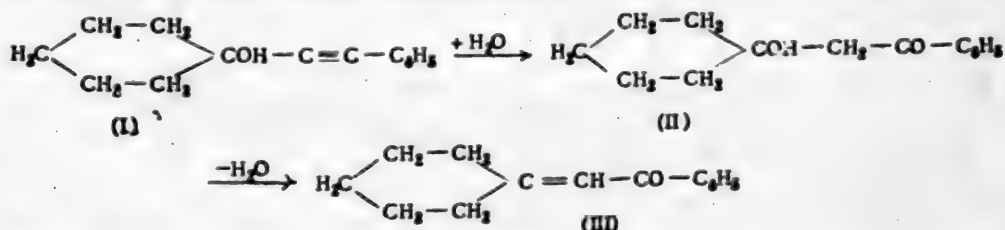
1-Phenylacetylenylcyclohexanol-1 was first synthesized by Zh. I. Iosich [2], and then later by foreign chemists [3] who dehydrated this alcohol with potassium bisulfate to prepare 1-phenylacetylenylcyclohexene-1.

On heating 1-phenylacetylenylcyclohexanol-1 at 60-65° with mercuric sulfate in the presence of dilute sulfuric acid (conditions completely analogous to those reported in Communication I [1]), only the unsaturated ketone, cyclohexylideneacetophenone (III) was obtained. Neither  $\alpha$ - or  $\beta$ -ketoalcohols, nor unsaturated ketones with a double bond in the polymethylene ring [4, 5] were detected in this case.

The mechanism of the transformation of 1-phenylacetylenylcyclopentanol-1 into cyclopentylideneacetophenone [1] remained open. The unsaturated ketone could have formed by the isomerization of the acetylenyl alcohol with a shift of the hydroxyl group into the  $\beta$ -position, or as a result of the elimination of water from the product of the hydration of the acetylenic alcohol, the  $\beta$ -ketol.

In order to solve this problem, the action of a more dilute mercuric sulfate, as well as various concentrations of sulfuric acid itself upon 1-phenylacetylenylcyclohexanol-1 were studied. It was found that a mixture of the unsaturated ketone and a hydroxyl-containing product was obtained under milder hydration conditions. This mixture was completely converted into cyclohexylideneacetophenone by treatment with sulfuric acid. In addition, it was shown that the acetylenyl alcohol was not converted into the ethylenic ketone by the action of sulfuric acid (15 and 30%), i.e., it did not undergo the acetylene-allene rearrangement.

Therefore, the unsaturated ketone (III) was obtained as a result of the hydration of the acetylenic alcohol (I) at the triple bond, and the subsequent dehydration of the  $\beta$ -ketol (II) formed as a result of the first reaction.



The dehydration is aided by the presence of the very active methylene group hydrogens in the chain of the molecule of the keto alcohol. The phenomenon was observed previously during the hydration of 3-phenylpropyne-2-ol-1 and 4,4-dimethylpentyne-2-ol-1, which finally formed unsaturated ketones with small amounts of the corresponding  $\beta$ -keto alcohols [6].

Upon comparison of the many literature reports on the hydration of tertiary acetylenic alcohols of the type  $RR_1COH-C\equiv CH$  in acidic media [1a] in the presence of mercuric sulfate, the following fact stands out: normal reaction products,  $\alpha$ -ketoalcohols ( $RR_1COH-CO-CH_3$ ), are formed with the presence of aliphatic radicals (R and  $R_1$  = alkyl) in these alcohols [7-12].

In the above case, because of the resemblance of polymethylene alcohols to the aliphatic, neither 1-phenylacetylenylcyclopentanol-1, nor 1-phenylacetylenylcyclohexanol-1 isomerize directly into ethylenic ketones by the action of an acidic mercuric sulfate solution, or in the presence of sulfuric acid alone. The presence of these ketones in the reaction products is explained by the dehydration of the  $\beta$ -ketoalcohol.

If one of the aliphatic radicals is substituted by an aryl, in addition to the hydration of the alcohol, an acetylene-allene rearrangement leading to the isomeric products, the unsaturated aldehydes, readily occurs [13]. The isomerization of purely aromatic tertiary acetylenic alcohols into unsaturated ketones by the action of sulfuric acid [14], or other acidic catalysts, is also reported in the literature [15].

Similar effects of the aromatic radicals on the acetylene-allene rearrangement were found by one of the authors during a study of the transformations of acetylenic pinacols of the type  $RR_1COH-COH(R_2)C\equiv CR_3$  by the action of sulfuric acid. In the case where  $R_2$  = aryl, the reaction products were found to be ethylenic  $\gamma$ -ketoalcohols (products of the acetylene-allene rearrangement), or the products of their further transformations [16-18]; where  $R_2$  = alkyl, the acetylene-allene rearrangement either did not take place at all [19], or was not the main direction of the reaction [20].

Of course, the structure of the molecule as a whole, the character of all the radicals, and their mutual distribution must be considered under identical conditions during an examination of the transformations.

Ultraviolet absorption spectra were made of cyclohexylideneacetophenone, cyclopentylideneacetophenone, reported in the previous communication [1], and for comparison, that of acetophenone. The absorption spectra were photographed in a quartz ISP-22 spectrograph. The absorption curves are given in the Figure.

The clear resemblance of curves I and II corresponding to cyclopentylidene- and cyclohexylideneacetophenone is apparent as well as their difference from curve III, corresponding to acetophenone. There are three general regions of absorption in the spectra of all three compounds: from 2400-2600, from 2600-2800, and 3000-3800 Å. The absorption spectra of cyclopentylidene- and cyclohexylideneacetophenone have greater absorption coefficients in comparison to acetophenone, and shifts of the main maxima of 20-30 Å toward the longer wavelengths.

The presence of an ethylenic bond was proved by means of infra-red absorption spectra on a Hilger D-88 spectrometer. The characteristic frequency band for the  $C=C$  bond lies in the region of 10.5  $\mu$ .

The spectrophotographic investigations were conducted in the Roentgenographic Laboratory of the Leningrad Institute of Technology under the direction of O. N. Setkina, whom the authors wish to thank for her aid and advice.

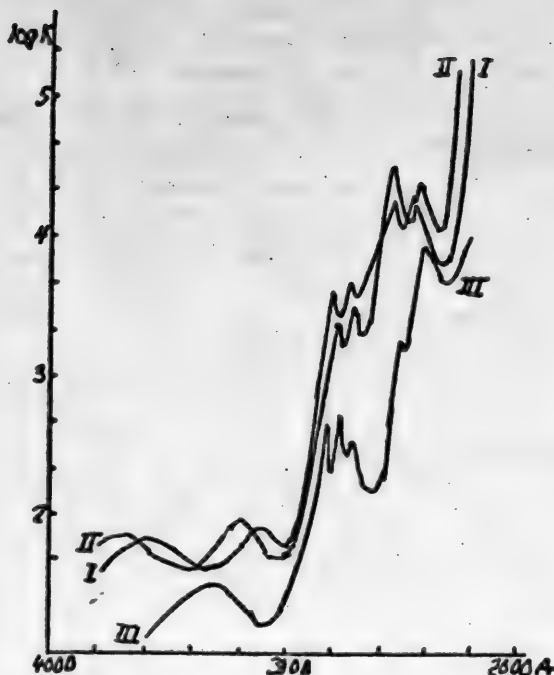
## EXPERIMENTAL

1-Phenylacetylenylcyclohexanol-1 was prepared according to Zh. I. Iosich's\* method. The purification of the alcohol was effected according to a previously reported method [1], i.e., solution of the substance in the minimum amount of methyl alcohol and precipitation with large excess of cold water. After two such purifications, long scale-like crystals with m.p. 61-62° were obtained, as reported in the literature [2, 3]. Yield, 36 g or 48% of the theoretical amount.

Experiment I. 1-Phenylacetylenylcyclohexanol-1 was heated for 2.5 hours to 60-65° with a four-fold excess of an aqueous solution of mercuric sulfate in sulfuric acid (10 g of  $HgO$  + 50 ml of  $H_2SO_4$  d 1.84, and 300 ml of  $H_2O$ ) [11].

Two analogous experiments were conducted in which 10 and 25 g of the acetylenyl alcohol were used. After heating, the mixture of water and the oily product was filtered from the suspended turbidity, and extracted 2 times with benzene, in which the turbidity was insoluble. After drying with sodium sulfate and the removal of the benzene, the residue was distilled at 140-140.5° (2 mm). A slightly greenish liquid with a pleasant odor was obtained, which immediately decolorized an aqueous potassium permanganate solution and a solution of bromine in chloroform, but which did not form methane upon reaction with methyl magnesium iodide. Yield, 80% of the theoretical amount.

\*G. A. Davydov participated in the synthesis of the alcohol.



Ultraviolet absorption spectra in n-hexane. I) Cyclopentylideneacetophenone, II) cyclohexylideneacetophenone, III) acetophenone.

g of the unsaturated ketone and 8.0 g of potassium permanganate were used (theory: 7.9 g of the oxidizing agent based on two moles of potassium permanganate per mole of the ketone); 300 ml of a 1% solution of potassium permanganate was added to the ketone with efficient stirring and the remaining 5 g of the oxidizing agent was added in dry form according to the decolorization of the solution. The oxidation proceeded without any external heating with a slight evolution of heat, and was finished within 2.5 hours. The manganese dioxide was filtered, washed with hot water, then ether, and an ether extraction of the filtrate was made. After the removal of the ether, 5.1 g of a light yellow liquid with a pleasant odor was obtained. A substance with b.p. 155° was obtained as the main fraction (1.8 g) upon distillation at ordinary pressure; upon further distillation a rapid rise of the temperature to 220° and a partial decomposition occurred. For this reason, the residue was distilled at 5 mm; b.p. 128-130°, 2.0 g. There was 4 g of a tar in the residue.

Fraction 1 with b.p. 155° at ordinary pressure formed a semicarbazone with m.p. 165-166° and a 2,4-dinitrophenylhydrazone with m.p. 160-162° corresponding to cyclohexanone [21] (mixed melting point).

Fraction 2 with b.p. 128-130° at 5 mm ( $n_D^{20}$  1.449) was a yellow liquid with a pleasant camphor-like odor, not containing a hydroxyl, decolorizing potassium permanganate and bromine, forming a semicarbazone (in alkaline medium) with m.p. 175-5-177° and a 2,4-dinitrophenylhydrazone with m.p. 129-130°.

0.2071 g substance: 12.31 g  $C_6H_6$ ;  $\Delta t$  0.49°. Found: M 172.  $C_{12}H_{12}O_2$ . Calculated: M 178.

Analysis of the 2,4-dinitrophenylhydrazone with m.p. 129-130°.

0.1065 g substance: 14.4 ml  $N_2$  (16°, 701 mm). Found %: N 15.73.  $C_{12}H_{12}C_4N_4$ . Calculated %: N 15.64.

According to properties and analysis of the 2,4-dinitrophenylhydrazone, the substance with b.p. 128-130° at 5 mm is cyclohexylidenecyclohexanone [22] formed as the result of a ketol condensation of cyclohexanone.

3.5 g of a precipitate (m.p. 99-105°) was formed by the acidification of the organic acid salts with dilute sulfuric acid. Benzoic acid with m.p. 120-121° was obtained by sublimation of the precipitate. After many

$d_4^{20}$  1.0577;  $d_4^{25}$  1.0436;  $d_4^{30}$  1.0418;  $n_D^{20}$  1.5736. Found:  $MR_D$  61.77.  $C_{14}H_{12}O^+$ . Calculated:  $MR_D$  60.61. 0.1407 g substance: 0.4328 g  $CO_2$ ; 0.1040 g  $H_2O$ . 0.2667 g substance: 11.48 g  $C_6H_6$ ;  $\Delta t$  0.6°. Found %: C 83.89; H 8.21; M 193.8.  $C_{14}H_{12}O$ . Calculated %: C 84.00; H 8.00; M 200.

The substance formed an orange precipitate at once with 2,4-dinitrophenylhydrazine, which showed a pyrazoline reaction. After recrystallization from boiling ethyl alcohol with the addition of ethyl acetate, the pyrazoline melted at 146-147°.

0.1203 g substance: 14.3 ml  $N_2$  (12°, 779 mm). 0.1002 g substance: 0.2313 g  $CO_2$ ; 0.0487 g  $H_2O$ . Found %: C 62.95; H 5.40; N 14.61.  $C_{12}H_{12}O_4N_4$ . Calculated %: C 63.17; H 5.26; N 14.74.

Twenty-four hours later, the substance with b.p. 140-140.5° at 2 mm solidified into a uniform white mass. After pressing on a porous plate and recrystallization from alcohol, the substance melted at 41-42° and gave the same pyrazoline (m.p. 146-147°) with 2,4-dinitrophenylhydrazine, as the liquid product with b.p. 140-140.5° at 2 mm. A determination of the molecular weight of the crystalline substance showed that it was the monomer.

0.1053 g substance: 15.09 g  $C_6H_6$ ;  $\Delta t$  0.17°. Found: M 205.  $C_{14}H_{12}O$ . Calculated: M 200.

Oxidation of the substance with m.p. 41-42°, 10

washings of the precipitate with water, benzoylformic acid was detected in the washings, which formed a difficultly water-soluble yellow phenylhydrazone with m.p. 152-153° (mixed melting point with authentic benzoylformic acid phenylhydrazone [23]). The aqueous solution in which benzoylformic acid was also detected, was subjected to steam distillation in order to decompose the benzoylformic acid and remove the formic; the residue was continually extracted with ether. The residue obtained after the removal of the ether, melted at 110-118° and consisted of benzoic acid with a small impurity of adipic acid according to the analysis of the silver salt.

0.0901 g salt. 0.0452 g Ag. 0.1030 g salt. 0.0517 g Ag. Found %: Ag. 50.17, 50.20.  $C_7H_5O_2Ag$ . Calculated %: Ag. 47.12.  $C_7H_5O_2Ag$ . Calculated %: Ag 59.96.

The products of the oxidation of the ethylenic ketone, cyclohexanone, cyclohexylidenecyclohexanone, benzoic acid, and benzoylformic acid confirmed the structure of the ketone as cyclohexylideneacetophenone.

**Experiment II.** 15 g of 1-phenylacetylenylcyclohexanol-1 and 60 ml of the hydrating agent (5 g HgO, 5 ml of  $H_2SO_4$  d 1.84, and 200 ml of  $H_2O$ ) were heated for 2.5 hours at 60-65°. After the usual isolation and three vacuum distillations at 2 mm, three fractions were obtained: 1) with b.p. 141-143°-2.2 g ( $n_D^{20}$  1.5775), 2) with b.p. 143-154°-5.6 g ( $n_D^{20}$  1.5750), 3) with b.p. 154-157°-5.3 g ( $n_D^{20}$  1.5700); residue -0.5 g.

All three fractions gave the same pyrazoline with m.p. 146-147° with 2,4-dinitrophenylhydrazine; they decolorized a solution of bromine in chloroform, whereby fraction 3 formed hydrogen bromide; all of the fractions decolorized an aqueous potassium permanganate solution, however, fraction 3 did not do it as rapidly as fraction 1; all reacted with methyl magnesium iodide with the formation of methane, but 3 was much more intense than 1.

Analysis of fraction 3 with b.p. 154-157° at 2 mm.

0.1038 g substance: 0.3044 g  $CO_2$ ; 0.0759 g  $H_2O$ . 0.0465 g substance: 2.5 ml  $CH_4$  (21°, 761 mm). 0.0439 g substance: 2.2 ml  $CH_4$  (21°, 761 mm). Found %: C 79.98; H 8.12; number OH group 0.48, 0.44.  $C_{14}H_{16}O$ . Calculated %: C 77.06; H 8.26; number OH group 1.

The analytical results and the properties showed that a mixture of the unsaturated ketone and the keto alcohol was obtained in this case.

All of the three fractions were combined, 10 g quantity, and treated with 15% sulfuric acid at 65-70° for 2 hours; 8.6 g of a substance with b.p. 142-143° at 3 mm and m.p. 41-42° was isolated, which corresponded to cyclohexylideneacetophenone.

**Experiment III.** 10 g of the acetylenic alcohol with m.p. 61-62° was heated for 2.5 hours to 65-70° with 200 ml of 15% sulfuric acid. After the usual isolation, 9.2 g of a thick liquid was obtained which rapidly crystallized. The substance reacted violently with methyl magnesium iodide with the formation of methane, and did not form a precipitate with a solution of 2,4-dinitrophenylhydrazine. After purification by means of reprecipitation by water from a methyl alcohol solution, the substance was isolated in the form of characteristic thin crystals with m.p. 61-62°, and was the starting acetylenic alcohol.

By the action of 30% sulfuric acid on 1-phenylacetylenylcyclohexanol-1 with heating up to 86° for 3 hours, the acetylenic alcohol was also unchanged.

#### SUMMARY

1. It was shown that 1-phenylacetylenylcyclohexanol-1 formed the isomeric ketone, cyclohexylideneacetophenone, by the action of mercuric sulfate in the presence of 8% free sulfuric acid, and a mixture of the unsaturated ketone and  $\beta$ -ketoalcohol by the action of that salt with 3% sulfuric acid.

2. It was shown that neither 15%, nor 30% sulfuric acid, without the mercuric salt, had any effect on the acetylenic alcohol.

3. It was shown, that the ethylenic ketone, formed under the conditions of G. M. Kucherov's reaction for tertiary polymethylene acetylenic alcohols (5- and 6-membered cycles), was a secondary product of the reaction, and was obtained as a result of the removal of water from the  $\beta$ -ketoalcohol product of the hydration of the acetylenic alcohols.

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\* In experiment I the concentration of free sulfuric acid corresponded to about 8%; in experiment II, 3%.  
\*\* See Consultants' Bureau English translation, page 1193.

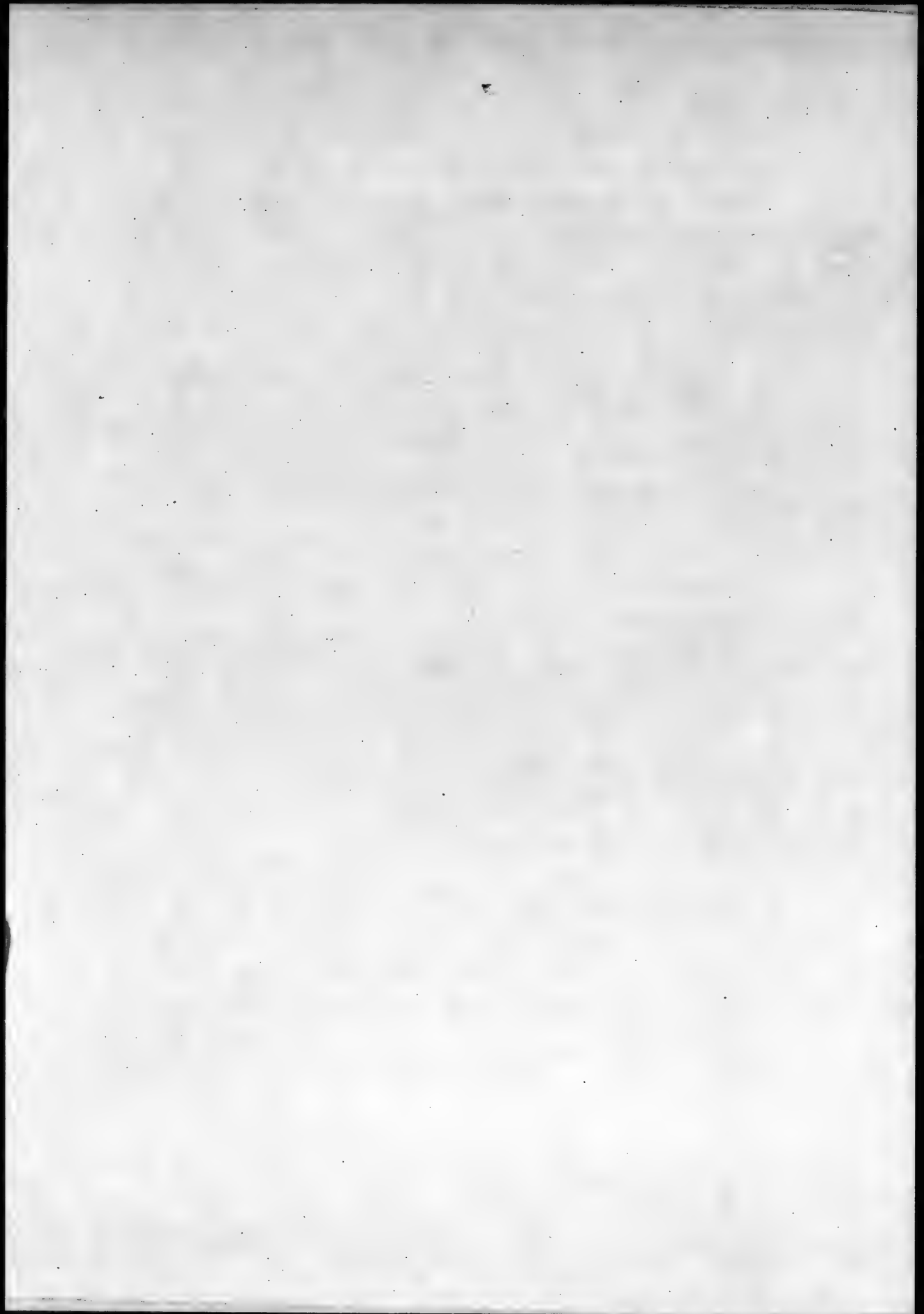


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Received March 2, 1953.

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  - \*\* See Consultants Bureau English translation page a-197.
  - \*\*\* See Consultants Bureau English translation page 87.
  - \*\*\*\* See Consultants Bureau English translation page 1605.
  - \*\*\*\*\* See Consultants Bureau English translation page 941.
  - \*\*\*\*\* See Consultants Bureau English translation page 2477.

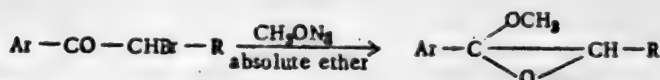


# INVESTIGATIONS OF CYCLIC ACETALS OF HYDROXYCARBOXYLIC COMPOUNDS

## V. METHYLLACTOLIDES OF ETHYLBENZOYLCARBINOL AND METHYL-*p*-ANISOYLCARBINOL

T. I. Temnikova and N. I. Almashi

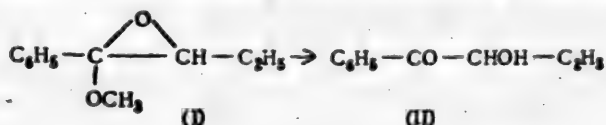
In order to further study the properties and transformations of lactolides of  $\alpha$ -ketoalcohols, the synthesis of the methyllactolides of two ketoalcohols, ethylbenzoylcarbinol and methyl-*p*-anisoylcarbinol was effected during the present investigation. Both of the methyllactolides were prepared by means of a method reported in the first communication of this series [1].



Where Ar = C<sub>6</sub>H<sub>5</sub>; R = C<sub>2</sub>H<sub>5</sub> and Ar = CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>; R = CH<sub>3</sub>.

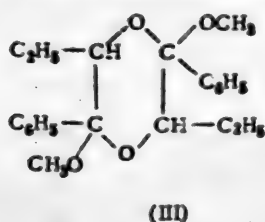
The methyllactolide of ethylbenzoylcarbinol (I) was considerably more stable than that of methylbenzoylcarbinol; however, upon distillation and storage, it slowly polymerized. The methyllactolide of methyl-*p*-anisoylcarbinol was very unstable, it polymerized rapidly upon standing in ether solutions in the presence of sodium methylate, upon distillation, and upon storage in pure form. Therefore, the introduction of a CH<sub>3</sub>O-group into the para position does not change the stability of the methyllactolide of methylbenzoylcarbinol; on the other hand, the substitution of a methyl by an ethyl directly at the oxide ring considerably increased the stability of the methyllactolide during distillation, as well as upon storage.

In order to prove the structure of the substance obtained by the action of sodium methylate upon  $\alpha$ -bromoethylphenyl ketone as the methyllactide, its hydrolysis in acidic medium was conducted:

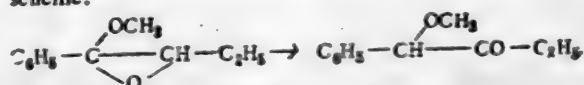


The isolated ethylbenzoylcarbinol (II) was identified and ultraviolet absorption curves of both compounds (the methyllactolide (I) and the ketoalcohol (II)) were taken. The absorption of ethylbenzoylcarbinol has maxima characteristic for benzoyl group (the Figure, Curve II) at a  $\lambda$  of 322 m $\mu$ , and  $\lambda$  280 m $\mu$  [2]. The methyllactolide does not have maxima in these regions, but it absorbs at the shorter wavelengths ( $\lambda$  265-242 m $\mu$ ) because of the presence of a benzene ring in it.

Because of the ease of hydrolysis in aqueous acidic medium, the methyllactolide of ethylbenzoylcarbinol formed the 2,4-dinitrophenylhydrazone of ethylbenzoylcarbinol by the action of a sulfuric acid solution of 2,4-dinitrophenylhydrazine. A dimerization occurred by the action of 1% HCl in methanol, and the cyclodimethyllactolide of ethylbenzoylcarbinol with m.p. 239-240° (III) was formed, which was previously reported [3].



An isomerization of the methyllactolide of ethylbenzoylcarbinol into a carbonyl-containing compound (Figure, Curve III) occurred by the action of magnesium bromide etherate: in analogy with previously studied cases, it can be supposed that the isomerization occurred according to the scheme:



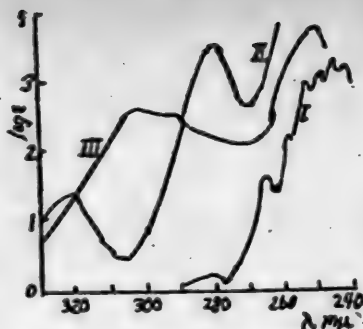
## EXPERIMENTAL

### I. Preparation of the Methyllactolide of Ethylbenzoylcarbinol.

38 g of  $\alpha$ -bromoethylphenyl ketone was added dropwise to a suspension of 8 g of sodium methylate in absolute ether. The mixture was left to stand for 24 hours, the sodium bromide and the excess sodium methylate were removed by filtration. The ether solution was vacuum distilled. 18 g of a substance with b.p. 94-95° at 10 mm resulted after two distillations. Yield, 65%.

$d_4^{20}$  1.0256;  $n_D^{20}$  1.49634;  $n_D^{25}$  1.4992;  $n_D^{28}$  1.50987;  $MR_\alpha$  50.76;  $MR_\beta$  51.93.  $C_{11}H_{14}O_2$ .

Calculated  $MR_\alpha$  50.52;  $MR_\beta$  51.65 (0.35 was added during the calculation as the increment for the oxide ring for the  $\alpha$  line, and 0.45 for the  $\beta$ ).



D) Methyllactolide of ethylbenzoylcarbinol. II) ethylbenzoylcarbinol. III) methyl ether of phenylpropionylcarbinol.

0.1349 g substance: 0.3663 g  $CO_2$ ; 0.0983 g  $H_2O$ . 0.1190 g substance: 0.3244 g  $CO_2$ ; 0.0858 g  $H_2O$ . 0.2060 g substance: 0.2779 g AgI. 0.0914 g substance: 15.71 g benzene:  $\Delta t$  0.17°. Found %: C 74.05, 74.33; H 8.16, 8.07;  $OCH_3$  17.8. M 176.  $C_{11}H_{14}O_2$ . Calculated %: C 74.11; H 7.92;  $OCH_3$  17.4; M 178.

The substance reacted violently with ethyl alcohol.

Reaction of the Methyllactolide of ethylbenzoylcarbinol with 2,4-dinitrophenylhydrazine. 0.5 g of the methyllactolide of ethylbenzoylcarbinol was added to a solution of 0.4 g of dinitrophenylhydrazine in 3 ml of concentrated sulfuric acid in 2 ml of water and 10 ml of alcohol. The mixture was left to stand overnight. Orange crystals deposited, which were recrystallized from light petroleum ether. M.p., 174-175°.

0.1168 g substance: 16.4 ml  $N_2$  (18°, 756 mm). Found %: N 16.81;  $C_{11}H_{14}O_5N_4$ . Calculated %: N 16.28.

The substance did not contain a methoxyl group.

Hydrolysis of the methyllactolide. 5 g of the methyllactolide was heated with 5% aqueous  $H_2SO_4$  for 6 hours. The hydrolysis product distilled completely at 90° at 2 mm. A glycol with m.p. 67-68° was obtained by the action of ethyl magnesium bromide on it. A mixed sample with glycol-3-phenylhexandiol-3,4 with m.p. 67-68° melted at the same temperature [4].

Reaction of the methyllactolide with methyl alcohol containing 2% HCl. 2 g of the methyllactolide was added dropwise with cooling to 20 ml of methyl alcohol containing 2% HCl. A frothing of the solution occurred; colorless crystals deposited as a result of the reaction, which were filtered and recrystallized from alcohol; m.p. 239-240°. 1.5 g was obtained.

Found %:  $OCH_3$  17.6  $C_{10}H_{12}O_2(OCH_3)_2$ . Calculated %:  $OCH_3$  17.41.

The crystals obtained melted without depression in a mixture with the cyclodimethyldilactolide of ethylbenzoylcarbinol reported previously [3], and obtained by the action of HCl in  $CH_3OH$  on ethylbenzoylcarbinol.

Isomerization of the methyllactolide of ethylbenzoylcarbinol into the methyl ether of phenylpropionylcarbinol. 4 g of the methyllactolide of ethylbenzoylcarbinol was added dropwise with efficient stirring to an ether solution of magnesium bromide prepared from 1.5 g of Mg [5]. Five hours later, the solution was washed with hydrochloric acid, alkali solution, and then after drying with  $MgSO_4$  it was distilled. 2 g of a substance boiling at 82° at 2 mm was obtained after two distillations.

0.1191 g substance: 0.3223 g  $CO_2$ ; 0.0864 g  $H_2O$ . 0.1039 g substance: 0.2827 g  $CO_2$ ; 0.0762 g  $H_2O$ . 0.0561 g substance: 18.6 ml 0.1 N.  $Na_2S_2O_3$ . Found %: C 73.86, 74.25; H 8.12 8.21;  $OCH_3$  17.21.  $C_{11}H_{14}O_2$ . Calculated %: C 74.13; H 7.91;  $OCH_3$  17.41.

### II. Preparation of the Methyllactolide of Methyl-p-anisoylcarbinol.

The starting substance for the synthesis, the  $\alpha$ -bromoethyl-p-anisyl ketone, obtained from anisole,  $\alpha$ -bromopropionylbromide, and  $AlCl_3$  had a b.p. 154-159° at 8 mm (Auer's gives a b.p. of 152-162° at 10 mm). The methyllactolide was obtained by the usual method [1,5] starting from 10 g of the bromoketone. A fraction 93-94° at 3 mm was obtained. Yield, 1.5 g.

A strong tarring occurred during the synthesis, as well as during distillation.

$d_4^{20}$  1.105;  $n_D^{20}$  1.50384;  $MR_\alpha$  51.96.  $C_{11}H_{14}O_3$   $\Gamma$ ,  $MR_\alpha$  51.73. 0.1226 g substance: 0.3067 g  $CO_2$ ; 0.0072 g  $H_2O$ . 0.1161 g substance: 0.2894 g  $CO_2$ ; 0.0722 g  $H_2O$ . 0.0496 g substance: 30.5 ml 0.1 N  $Na_2S_2O_3$ . Found %: C 68.16, 67.85; H 7.05, 6.93;  $OCH_3$  31.67.  $C_{11}H_{14}O_3$ . Calculated %: C 68.04; H 7.22;  $OCH_3$  31.95.

#### SUMMARY

1. The methyllactolides of ethylbenzoylcarbinol and methyl-p-anisoylcarbinol were newly obtained. The methyllactolide of ethylbenzoylcarbinol was comparatively stable, but it slowly polymerized upon storage. The methyllactolide of methyl-p-anisoylcarbinol polymerized very rapidly upon distillation, and upon being stored in the pure form.
2. The transformations of the methyllactolide of ethylbenzoylcarbinol were studied.

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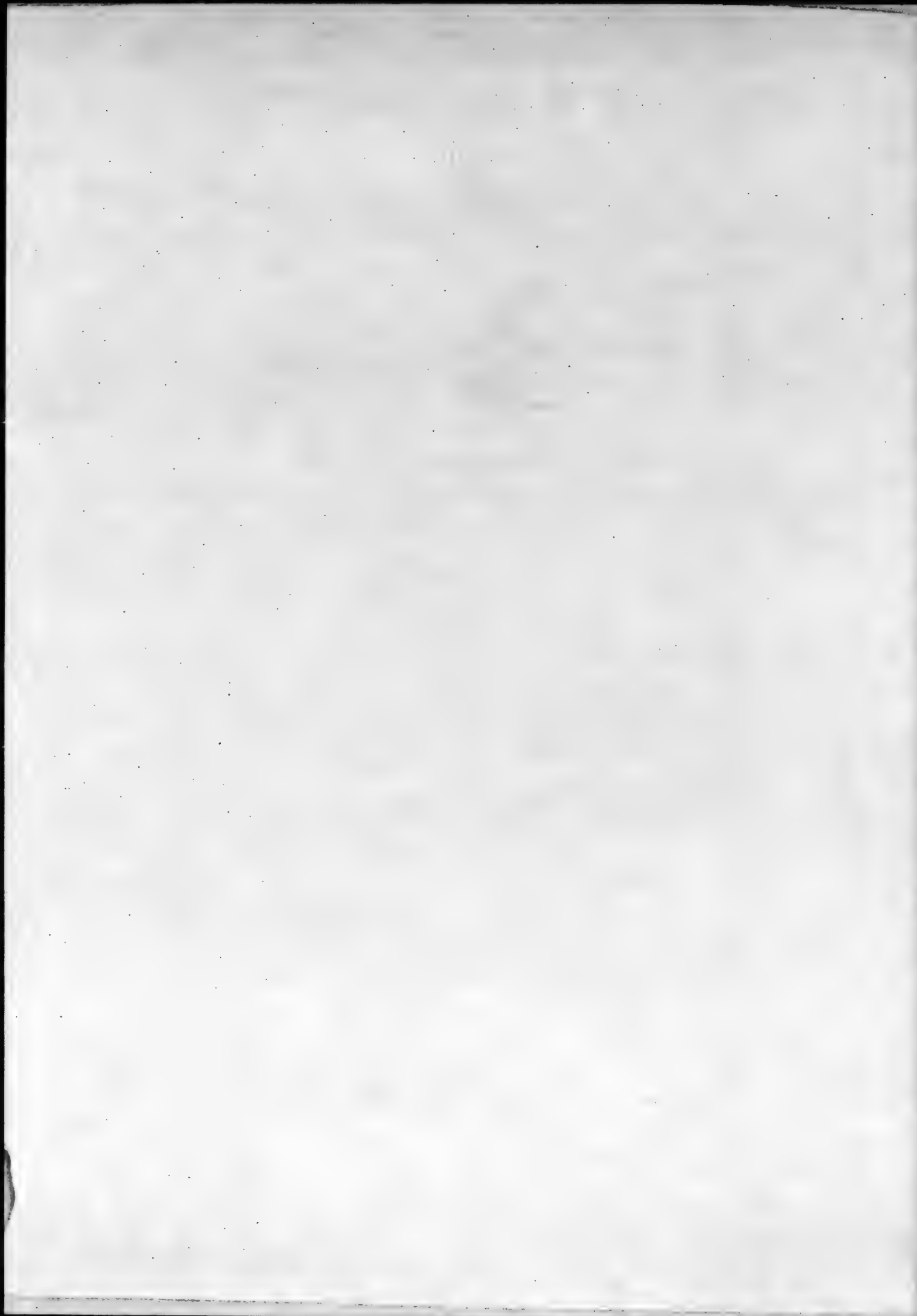
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Received April 20, 1953

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## ACYLATION OF UNSATURATED HYDROCARBONS

### II. ACETYLATION OF PHENYLACETYLENE AND HEPTYNE-1 WITH ACETIC ANHYDRIDE IN THE PRESENCE OF ZINC CHLORIDE

V. N. Belov and G. Z. Shekhtman

In the first communication of the authors and Rudol'fi [1], it was shown that 2-chloro-1-acetylcyclohexane was formed, in addition to tetrahydroacetophenone, during the acetylation of cyclohexene with acetic anhydride in the presence of chlorides of certain metals (zinc and stannic chlorides). It was shown that the intermediate formation of acetyl chloride or hydrogen chloride did not occur under the conditions of this reaction. On the basis of these results, which indicated that a direct transfer of the chlorine atom from the condensing medium, (metal chloride) to the ketone formed occurred, during the process of the reaction, a general scheme of this reaction was suggested.

In order to obtain supplementary experimental material on the given problem, the acetylation of certain hydrocarbons containing a triple bond, namely, phenylacetylene and heptyne-1, was effected under similar conditions (acetic anhydride in the presence of zinc chloride). In both cases only the corresponding chloroketones with an ethylenic bond could be isolated: 1-chloro-1-phenylbuten-1-one-3 (I;  $R=C_6H_5$ ) in the case of the acetylation of phenylacetylene (yield about 31% of the theoretical), and 4-chlorononen-3-one-2 (II;  $R=C_8H_{17}$ ) for the acetylation of heptyne-1 (yield about 20% of the theoretical). Acetylenic ketones were not detected among the reaction products. These results may be described by the following general scheme:



Products were obtained in these experiments on the acetylation of acetylenic hydrocarbons with acetic anhydride in the presence of zinc chloride, which were usually formed by the reaction of acetylenic hydrocarbons with acetyl chloride in the presence of aluminum chloride. The last reaction leads, as it is known, to the formation of products of the addition of acetyl chloride to the hydrocarbon with the triple bond [2]. Chloroketone (II) was also obtained by this method, and was found to be identical with that obtained by acetylation with acetic anhydride. The only difference was in the yield of the chloroketone (in the reaction with acetyl chloride in the presence of  $AlCl_3$  the yield was about 45% of the theoretical).

The results obtained in the present investigation are completely in accordance with the mechanism of the acetylation reaction of unsaturated hydrocarbons with acetic anhydride in the presence of metal chlorides suggested in the first communication on this problem [1]. It is believed that the process occurs by means of an intermediate formation of a complex consisting of all three components of the reaction mixture. Such an intermediate complex can be formed, for example, by the reaction of acetic anhydride with the molecular compound formed by the unsaturated hydrocarbon and the metal chloride, as well as by the reaction of the unsaturated hydrocarbon with the molecular compound formed by the acetic anhydride and the metal chloride. If, in the case of the acetylation of the ethylenic hydrocarbon, the intermediate complex is capable of decomposing with the formation of the saturated chloroketone, as well as the unsaturated ketone not containing a chlorine, then with acetylenic hydrocarbons, a similar complex decomposes exclusively in the direction of the formation of the chloroketone. This, however, does not exclude the possibility that the  $\beta$ -chloroketone may be the main product of the acetylation of ethylenic hydrocarbons, but, because of its instability, is readily transformed into the unsaturated ketone (for example, it gives a hydrogen chloride fragment to a molecule of the starting ethylenic hydrocarbon).

The considerably smaller activity of the chlorine atom in the unsaturated chloroketones (I) and (II) obtained, in comparison with that of the  $\beta$ -chlorovinylketones obtained from acetylene itself, must be mentioned.

As it is known, a chlorine atom in  $\beta$ -chlorovinylketones obtained by the addition of acyl halides to acetylene, possesses very great reactivity. This fact causes, for example, instability, and in isolated cases,

because of this instability, makes the preparation of certain derivatives impossible for  $\beta$ -chlorovinyl ketones. Thus, according to the data of Yakubovich and Merkulova [2],  $\beta$ -chlorovinyl ketone semicarbazones change very easily which hinders their purification by recrystallization. The impossibility of obtaining the oxime and the hydrazone of methyl- $\beta$ -chlorovinyl ketone was mentioned in the earlier communication of Cornillot and Alquier [3]. Recently, Nesmeyanov, Kochetkov, and Rybinskaya [4] showed that the reaction of alkyl- $\beta$ -chlorovinyl ketones with hydrazine, as well as with arylhydrazines, leads to the formation of the 3-alkyl- and the 1-aryl-3-alkylpyrazolones which result from the participation of the chloro- as well as the carbonyl group in the reaction. This property of  $\beta$ -chlorovinyl ketones was used by Nesmeyanov and Kochetkov [5] for the synthesis of certain heterocyclic compounds based upon them. In particular, they, together with Semenov [6], developed a convenient method for the preparation of isoxazoles by the reaction of  $\beta$ -chlorovinyl ketones with hydroxylamine.

All of the above literature data are in relation to chlorovinyl ketones without substituents in the chlorovinyl radical. A considerably greater stability for the bond with the chlorine atom was found in both of the substituted  $\beta$ -chlorovinyl ketones (I and II) containing the amyl and phenyl group, respectively, on the carbon atom bound directly to the chlorine atom.

4-Chlorononene-3-one-2, as well as 1-chloro-1-phenylbuten-1-one-3, formed completely stable semicarbazones which did not change during many recrystallizations. A pure preparation of this chloroketone was obtained, by using the general method of decomposition (see the experimental section), from the semicarbazone of 1-chloro-1-phenylbuten-1-one-3. Both of the chloro ketones (I and II) formed other characteristic ketone derivatives retaining the chlorine atom in the molecule. Thus, oximes were obtained for ketones (I) and (II), and 2,4-dinitrophenylhydrazone for (I). These derivatives also did not show any noticeable signs of changing upon recrystallization, or upon prolonged storage. Only the oximes of the chloroketones were formed by conducting the reaction of these chloroketones with hydroxylamine under conditions which were used by Nesmeyanov and Kochetkov for the preparation of isoxazoles; heterocyclic compounds were not found among the reaction products.

Phenylpropionic acid was obtained by the oxidation of the chloroketone, obtained by the reaction of phenylacetylene with acetic anhydride in the presence of zinc chloride, with sodium hypochlorite. \*

Therefore, the oxidation process was accompanied by the elimination of a hydrogen chloride fragment.

## EXPERIMENTAL

### 1. Reaction of Phenylacetylene with Acetic Anhydride in the Presence of Zinc Chloride.

23 g of anhydrous zinc chloride was added gradually with stirring to a mixture of 35 g of phenylacetylene (b.p. 142-143°,  $n_D^{20}$  1.5472,  $d_4^{20}$  0.9340) and 52 g of acetic anhydride. The temperature of the mixture rose from 60-80°. After the temperature dropped, the reaction mixture was heated on the water bath until complete solution of the zinc chloride, which required about 3 hours. After steam distillation of the volatile reaction products and their subsequent fractionation, (about 10.6 g of starting phenylacetylene (~30% of that used) and 13.5 g of a ketonic fraction with b.p. 132-138° (10 mm), the main part of which distilled at 132-135° (10 mm), were obtained. The chlorine content in this fraction was 18.8% (calculated for  $C_{10}H_7OCl$  19.63%); the ketone content (determined by the oxidation method) based on the chloro-ketone, was 97%. The semicarbazone, obtained from this fraction, had an m.p. 180.5-181° (from alcohol).

Found: N 18.13.  $C_{10}H_7ON_3Cl$ . Calculated %: N 17.67.

A pure preparation of 1-chloro-1-phenylbuten-1-one-3 with b.p. 137-138° (10 mm) was obtained by the decomposition of the semicarbazone (heating with an aqueous oxalic acid solution with the simultaneous solution of the ketone).

$n_D^{20}$  1.5930;  $d_4^{20}$  1.2373.  $MR_D$  49.47.  $C_{10}H_7OCl$ . Calculated:  $MR_D$  49.19.

Found %: C 66.63, 66.62; H 4.90, 5.02; Cl 19.52.  $C_{10}H_7OCl$ . Calculated %: C 66.49; H 5.02; Cl 19.63.

The oxime, colorless needles, m.p. 93° (from alcohol).

Found %: C 61.35, 61.16; H 5.23, 5.21; N 7.26, 7.25; Cl 18.01, 18.16.  $C_{10}H_{11}ONCl$ . Calculated %: C 61.38; H 5.16; N 7.16; Cl 18.12.

The 2,4-dinitrophenylhydrazone, shining red crystals, m.p. 194-195° (from alcohol).

\* The oxidation was conducted in order to prove the structure of the ketone as 1-chloro-1-phenylbuten-1-one-3.

Found %: C 53.46, 53.63; H 3.80, 3.67; N 15.74, 15.46; Cl 10.13, 10.14.  $C_9H_9O_2N_2Cl$ . Calculated %: C 53.27; H 3.63; N 15.53; Cl 9.83.

Oxidation of 1-chloro-1-phenylbuten-1-one-3 with sodium hypochlorite. 400 ml of a sodium hypochlorite solution (containing 4.5% active chlorine) was added with continuous stirring over a 15-minute period to 8 g of the chloroketone (b.p. 133-135° at 10 mm,  $n_D^{20}$  1.5930). The mixture was then stirred for 3 hours at 50-60°. The unreacted ketone (about 2 g) was extracted with benzene from the reaction mixture. 3.8 g of a crystalline product was obtained by the acidification of the evaporated aqueous solutions. After two recrystallizations from water, colorless, shiny needles with m.p. 138° were obtained. A mixed melting point with an authentic preparation of phenylpropionic acid showed no depression.

Found acid number: 384.  $C_9H_9O_2$ . Calculated acid number: 383.2. Found %: C 73.91, 73.54; H 4.27, 4.45.  $C_9H_9O_2$ . Calculated %: C 73.98; H 4.14

## 2. Reaction of Heptyne-1 with Acetic Anhydride in the Presence of Zinc Chloride.

9 g of anhydrous zinc chloride (with efficient stirring) was added to a mixture of 20 g of heptyne-1 (m.p. 99-103°,  $n_D^{20}$  1.4200, containing 76% of the 1-isomer)\*. An increase in the temperature occurred which was decreased by water cooling. For complete solution of the zinc chloride, the reaction mixture was heated for 3 hours at 50-55° with continuous stirring. The reaction product was then poured into water and extracted with ether. The extract was washed with sodium carbonate solution and with water, and then dried with sodium sulfate. After removal of the solvent and fractionation of the residue in vacuum, 5 g of the starting substance and 5.5 g of a fraction with b.p. 93-95° (10 mm) were obtained

$n_D^{20}$  1.4645;  $d_4^{20}$  0.9939; found  $MR_D$  48.54% Cl 26.10.  $C_9H_{15}OCl$ . Calculated:  $MR_D$  48.17; % Cl 20.30.

Semicarbazone, colorless crystals, m.p. 137-138° (from alcohol).

Found %: N 18.11, 18.13.  $C_{10}H_{17}ON_2Cl$ . Calculated %: N 18.14.

A mixed melting point with the semicarbazone of the chloro-ketone obtained by the reaction of heptyne with acetyl chloride in the presence of aluminum chloride gave no depression.

An oxime was obtained by heating 1.2 g of 4-chlorononene-3-one-2 with a solution of 0.8 g of hydroxylamine hydrochloride in 10 ml of methanol for 3 hours on the water bath. The reaction mixture was diluted with 4 volumes of water, the oily layer extracted with ether. The solution was dried with sodium sulfate; after removal of the solvent, the residue was vacuum distilled. A product with b.p. 85-86° (10 mm) was obtained;  $n_D^{20}$  1.4687.

Found %: N 7.41, 7.34; Cl 18.77, 18.69.  $C_9H_{15}ONCl$ . Calculated %: N 7.39; Cl 18.69.

The same oxime with b.p. 85-86° (10 mm) was obtained by conducting the reaction in the presence of sodium acetate. The nitrogen content of this oxime also corresponded to the calculated.

## SUMMARY

1. It was found that chloroketones with ethylenic bonds (1-chloro-1-phenylbuten-1-one-3, and 4-chlorononene-3-one-2) were formed by the reaction of phenylacetylene and heptyne-1 with acetic anhydride in the presence of zinc chloride. Acetylenic ketones were not found among the reaction products.

2. These results prove the expressions of the mechanism of the acetylation reactions of unsaturated hydrocarbons with acetic anhydride in the presence of metal chlorides stated in the first communication.

3. The lesser reactivity of the chlorine atom in 1-chloro-1-phenylbuten-1-one-3 and 4-chlorononene-3-one-2 in comparison to that of the chlorine in 3-chlorovinylketones not containing substituents on the carbon, to which the chlorine atom is directly connected, was shown.

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Received April 4, 1953.

The All-Union Scientific Research Institute  
for Synthetic and Natural Fragrant Substances

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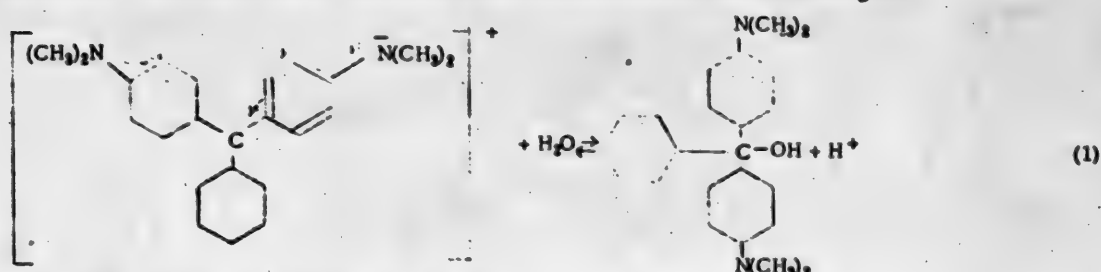
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# DISSOCIATION OF TRIARYLCARBINOLS

O. F. Ginsburg

As early as the 90's it had been shown that basic triphenylmethane dyes were subjected to hydrolysis in aqueous solution [1]. As a result of the hydrolysis, a chemical equilibrium is gradually established in the solution, which, for example, can be represented by the following equation for malachite green:



From equation (1) it follows that the quantitative study of the hydrolysis reaction would make possible the determination of the dissociation constant of the so-called carbinol bases of the triphenylmethane dyes, which are formed by the removal of a hydroxyl group from the methane carbon atom.

The hydrobromide and hydroiodide of malachite green were obtained in chemically pure form [2], and the pH of their aqueous solutions was determined at  $19 \pm 1^\circ$ . The values found are given in Table 1.

TABLE 1

Expt. No.	Name of dyes	C (moles/liter)	pH value	
			Found	Calculated for $250^\circ$
1	Malachite green hydrobromide .....	$1.48 \cdot 10^{-3}$	4.95	4.86
2	Malachite green iodide .....	$1.05 \cdot 10^{-3}$	5.02	4.94
3	Crystal violet hydrobromide .....	$7.45 \cdot 10^{-4}$	6.40	6.25
4	Crystal violet iodide .....	$9.60 \cdot 10^{-4}$	6.35	6.19

Comparatively recently, Goldacre and Phillips [2], on the basis of the experimental results obtained by a comparison of the intensities of the colors of aqueous solutions of the dyes at various pH, calculated characteristics called by them "ionization constant at equilibrium" for a whole series of basic triphenylmethane dyes, which also are hydrolysis constants of the dyes. pH values were calculated using these constants, which must correspond to those of the investigated solution.

As it is apparent from Table 1, the values found and calculated are very close, and for this reason the dissociation constants of 4,4'-tetramethyldiaminotriphenylcarbinol and 4,4',4''-hexamethyltriaminotriphenylcarbinol calculated on the basis of the pH value of the solution of the dyes and on the experimental results obtained by Goldacre and Phillips also agree satisfactorily with each other. It was found that the dissociation constants of 4,4'-tetramethyldiaminotriphenylmethylecarbinol was equal to  $9.24 \cdot 10^{-8}$ , and  $3.76 \cdot 10^{-8}$  for 4,4',4''-hexamethyltriaminotriphenylcarbinol (at  $19^\circ$ ).

Continuing the study of the hydrolysis of salts, from which the so-called "pseudobases" are formed by the action of alkalies, it appeared to be of interest to compare the hydrolysis constants of these salts in various solvents. For this purpose, the hydrolysis constants of 4,4'-tetramethyldiaminotriphenylcarbinol, 4,4'-tetramethyldiaminodiphenylcarbinol, diantipyrylphenylcarbinol, and 10-methyl-9-phenyl-9-hydroxy-9,10-dihydroacridine salts were determined in aqueous acetone. Hydrolysis constants were calculated from the pH values of aqueous acetone solutions containing equimolecular amounts of the carbinol and its salt. Table 2 compares the pK of the above compounds

in aqueous acetone and in water.

It must be mentioned that the hydrolysis constant of malachite green was calculated on the basis of experimental data obtained in the following experiment: a sample of 4,4'-tetramethyldiaminotriphenylcarbinol was dissolved in a defined quantity of aqueous acetone.

TABLE 2

Expt. No.	Name of carbinol	pK	
		in water	in aqueous acetone
1	4,4'-Tetramethyldiaminodiphenylcarbinol	5.61*	4.70
2	Diantipyrilphenylcarbinol	6.56	5.50
3	4,4'-Tetramethyldiaminotriphenylcarbinol	7.07	6.05
4	10-Methyl-9-phenyl-9-hydroxy-9,10-dihydroacridine	9.58	8.55

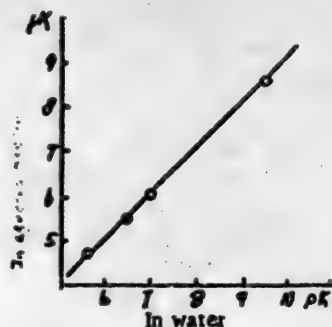
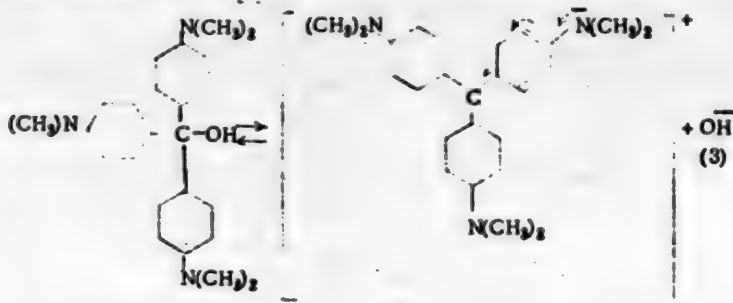
When equilibrium was established in the solution obtained, the concentration of hydrogen ions was determined potentiometrically, and that of the dye cations colorimetrically, while the pK was calculated by

means of formula (2), and was found to be equal to 6.06, i.e., completely satisfactorily agreed with the values given in Table 2.

$$pK = pH - \log \frac{[ROH]}{[R^+]}. \quad (2)$$

Since the hydrolysis of the above compounds is a special case of an acid-base equilibrium, and for this reason, as it was expected in view of Brønsted's theory [3], the points obtained, upon plotting the pK values in aqueous acetone solution versus those in water on coordinate axes, lie with complete agreement upon a straight line, the tangent of an angle of inclination equal to 1 (see the figure).

It could be expected that, in contrast to aqueous solutions, in nitrobenzene in which solvation is impossible and which is accompanied by the transformation of the cation of the dye into a compound with a 4-covalent methane carbon atom, the dissociation of the carbinol could be very considerable. The experiments conducted confirmed these suggestions. Thus, for example, nitrobenzene solutions of 4,4'-tetramethyldiaminotriphenylcarbinol and 4,4',4''-hexamethyltriaminotriphenylcarbinol were prepared, in which the first compound was found to be dissociated to an extent of 70%, and the second, 90%.



Therefore, the results obtained in the present investigated completely confirm the suggestions of the ability of the so-called pseudo bases of Hantzsch to dissociate in various solvents with the cleavage of the hydroxyl group. This dissociation, for example, can be represented by equation (3) for 4,4',4''-hexamethyltriaminotriphenylcarbinol.

## EXPERIMENTAL

### 1. 4,4'-Tetramethyldiaminotriphenylcarbinol

0.1001 g of 4,4'-tetramethyldiaminotriphenylcarbinol was dissolved in 70 ml of 60% aqueous acetone.

Concentration of the solution,  $C = 4.13 \cdot 10^{-3}$  moles/liter, pH of the solution, 8.50, temperature,  $19 \pm 1^\circ$ . The absorption spectrum of the solution is given in Table 3.

\* According to the results of Goldacre and Phillips [2].

TABLE 3\*

$\lambda$ m $\mu$	D	$\lambda$ m $\mu$	D	$\lambda$ m $\mu$	D
500.0	0.024	605.0	0.490	630.0	0.675
520.0	0.035	620.0	0.852	635.0	0.612
540.0	0.074	622.5	0.879	640.0	0.531
560.0	0.150	625.0	0.690	650.0	0.345
580.0	0.257	627.5	0.686		

TABLE 4

$\lambda$ m $\mu$	D	$\lambda$ m $\mu$	D	$\lambda$ m $\mu$	D
520	0.008	600	0.212	630	0.365
540	0.027	610	0.295	640	0.285
560	0.070	620	0.366	650	0.178
580	0.131	625	0.375		

The solution obtained was acidified with a 0.1 N hydrochloric acid solution and diluted 500 times with 60% aqueous acetone. On the following day, the absorption spectrum of the dye solution obtained was taken, whose pH was 4.50 (temperature  $19 \pm 1^\circ$ ). The concentration of the dye in the solution was  $C 0.82 \cdot 10^{-6}$  moles/liter.

The absorption spectrum of the solution obtained is given in Table 4.

## 2. Determination of the pH of Aqueous Solutions of Several Dyes

A sample of the salt was dissolved in water. The pH of the solution was measured in all experiments on a pH meter with glass and calomel electrodes at  $19 \pm 1^\circ$ . The results obtained are given in Table 5.

TABLE 5

Expt. No.	Name of the dissolved substance	Sample (in g)	Amount of water (ml)	pH
1	Malachite green hydrobromide	0.0607	100	4.95
2	Malachite green hydroiodide	0.0481	100	5.02
3	Crystal violet hydrobromide	0.0505	150	6.40
4	Crystal violet hydroiodide	0.0479	100	6.35
5	Antipyrine orange nitrate	0.0797	100	4.70
6	10-Methyl-9-phenylacridinium iodide	0.0900	100	6.10
		0.0912	100	6.10

## 3. Determination of the pH of Several Salts in Aqueous Acetone

A sample of the substance was dissolved in 70 ml of 60% aqueous acetone. If the salt was used, 0.5 equivalents of sodium hydroxide was added; if the bases were used, 0.5 equivalents of hydrochloric acid. On the following day, the pH of the solution was determined at  $19 \pm 1^\circ$ . The results obtained are given in Table 6.

TABLE 6

Expt. No.	Name of the dissolved substance	Sample	Addend of 0.1 N sol. (ml)		pH
			HCl	NaOH	
1	Malachite green hydroiodide	0.0588	—	0.72	6.06
2	4,4'-Tetramethyldiaminotriphenylcarbinol	0.1886	2.72	—	6.05
3	Antipyrine orange nitrate	0.1004	—	0.95	5.50
4	Diantiprylphenylcarbinol	0.1231	1.28	—	5.50
5	4,4'-Tetramethyldiaminodiphenylcarbinol	0.1102	2.04	—	4.70
6	10-Methyl-9-phenylacridinium iodide	0.1448	—	1.82	8.60
		0.1515	2.64	—	8.60
7	10-Methyl-9-phenyl-9-hydroxy-9,10-dihydroacridine	0.1517	2.64	—	8.50
		0.1523	2.65	—	8.55

## 4. Absorption Spectra of Solutions of the Dyes and their Carbinol Bases in Nitrobenzene

a) 4,4'-Tetramethyldiaminotriphenylcarbinol and malachite green hydroiodide were dissolved in nitrobenzene. The solutions obtained were heated for 2 hours on the water bath at  $80^\circ$ , cooled, and the absorption spectra taken on the following day (Table 7).

The applicability of Beer's law to solutions of malachite green in nitrobenzene was shown previously [4].

The concentration of the dye cation in the nitrobenzene solution of 4,4'-tetramethyldiaminotriphenylcarbinol was equal to  $4.0 \cdot 10^{-5}$  g-tons/liter.

b) Solutions of 4,4',4"-hexamethyltriaminotriphenylcarbinol and crystal violet hydroiodide in nitrobenzene were prepared. The absorption spectra were taken 3 days later (Table 8).

The concentration of the dye cation in the nitrobenzene solution of 4,4',4"-hexamethyltriaminotriphenyl-

\* All of the spectrophotometric measurements were effected on the SF-11 spectrophotometer.

carbinol was equal to  $7.2 \cdot 10^{-8}$  g-ions/liter.

TABLE 7

$\lambda$ m $\mu$	D	
	Malachite green hydroiodide $C = 4.3 \cdot 10^{-5}$ moles/liter	4,4'-Bis(4-dimethyl- aminotriphenyl)carbinol $C = 5.8 \cdot 10^{-5}$ moles/liter
600	0.42	0.40
620	0.85	0.81
630	1.09	1.04
635	1.15	1.09
640	1.06	1.01
650	0.79	0.75

TABLE 8

$\lambda$ m $\mu$	D	
	Crystal violet hydroiodide $C = 5 \cdot 10^{-5}$ moles/liter	4,4',4''-Trimethyltri- aminotriphenylcarbinol $C = 8 \cdot 10^{-5}$ moles/liter
550	0.237	0.444
590	0.450	0.670
600	0.497	0.720
605	0.468	0.700
610	0.468	0.658
620	0.381	0.502

### SUMMARY

The carbinol compounds of the triarylmethane dyes (the so-called "pseudo bases" of Hantzsch) are capable of dissociation with the cleavage of the hydroxyl group and the formation of dye cations. This dissociation occurs in other solvents, as well as in water.

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Received December 25, 1952.

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## CYCLOALKYLATION OF AROMATIC COMPOUNDS

### VII. CONDENSATION OF CYCLOHEXANOL WITH CHLOROBENZENE

N. G. Sidorova and I. S. Lapovok

In the previous investigations [1], it was shown that the alkylation of aromatic hydrocarbons with cyclic alcohols in the presence of aluminum chloride gave good yields of monoalkylated products. It seemed of interest to try this method upon the halobenzenes, and in particular, upon chlorobenzene. For this reason, the study of the condensation of chlorobenzene with cyclohexanol in the presence of aluminum chloride was conducted. In order to compare the various methods of alkylation, the alkylation of chlorobenzene with cyclohexene in the presence of aluminum chloride and with cyclohexanol in the presence of phosphoric acid was also studied.

The cycloalkylation of the halobenzenes has been studied many times in the past. Their condensation with cyclohexanol in the presence of  $\text{AlCl}_3$  [2],  $\text{H}_2\text{SO}_4$  [3], and  $\text{BF}_3$  [4] has been reported. The maximum yields (34-50% of theory) were obtained by the alkylation of chlorobenzene, the lowest, with the alkylation of iodobenzene. In both cases, only the obtaining of the p-isomers is reported.

The condensation of halobenzenes with cyclohexene was effected in the presence of  $\text{AlCl}_3$  [5, 6] and  $\text{H}_2\text{SO}_4$  [7]. The systematic study of the reaction in the presence of sulfuric acid conducted by Truffault is of the greatest interest. However, even under optimum conditions the yield of the p-cyclohexylbenzene by means of this reaction did not exceed 44% of theory. Similar yields were obtained with the condensation under the influence of aluminum chloride. Considerably better results (72% of p-cyclohexylchlorobenzene and 65% of p-cyclohexylbromobenzene) were obtained by the use of chlorocyclohexane and  $\text{AlCl}_3$  [8]. An analogous condensation of bromobenzene with chlorocyclohexane was also effected [9]. This investigation is of interest because the authors investigated the reaction products in detail and showed that they consisted of all three isomers of cyclohexylbromobenzene, whereas all of the other investigators reported only the obtaining of p-cyclohexylhalobenzenes. It is interesting that the formation of o- and m-isomers, in addition to the p-isomers, has been frequently observed during the alkylation of halobenzenes with aliphatic compounds [10].

The alkylation of chlorobenzene with cyclohexanol in the presence of aluminum chloride was studied in greater detail. The aim of this investigation was not only to find those conditions which would lead to good yields of alkylation products, but also the effect of the conditions upon the formation of the different isomers. 0.9-1.0 moles  $\text{AlCl}_3$  per mole of cyclohexanol was necessary for the obtaining of good yields. A favorable effect was shown by an excess of chlorobenzene and by a decrease in temperature. The temperature affects not only the yields of the alkylation products, but also their compositions: the product obtained at high temperatures consisted wholly of p-cyclohexylchlorobenzene, while that obtained by condensation at  $0^\circ$ , contained considerable amounts of the o-isomer. The order of the addition of the reactants was of great effect. Better results were obtained when the  $\text{AlCl}_3$  was added gradually to a mixture of chlorobenzene and cyclohexanol. Considerable amounts of higher boiling products and tars were obtained when cyclohexanol was added to a mixture of chlorobenzene and aluminum chloride, in addition to cyclohexylchlorobenzene. This is explained by the fact that, with the gradual addition of the alcohol, the first portions of it come in contact with a large amount of aluminum chloride, whose excess usually leads to accumulation of poly-substituted products. Under optimum conditions, as high as 85% yields of cyclohexylchlorobenzene were attained.

The identification of the reaction products was effected by oxidizing them to the chlorobenzoic acids. In one case, the method of dehydrogenation with bromine, usually used for cyclic hydrocarbons [11], was applied. Its use for the dehydrogenation of cyclohexylchlorobenzene gave good results.

The product obtained by condensation at  $95^\circ$  was the pure p-isomer, since only p-chlorobenzoic acid was obtained upon oxidation with nitric acid. The condensation product at  $0^\circ$  consisted of approximately 2/3rds of the p- and 1/3rd of cyclohexylchlorobenzene, which was shown by its oxidation to the corresponding chlorobenzoic acids. The product obtained at  $20^\circ$  was a mixture of o- and p-isomers with the latter predominating. The m-isomer could not be detected in any case.



The following were varied during the condensation of chlorobenzene with cyclohexene in the presence of aluminum chloride: the amount of catalyst and chlorobenzene, the order of addition of the reagents, and the reaction time. However, the change of the conditions had little effect upon the results in this case. The product was obtained in low yield (17-26% of the theoretical amount) and always contaminated with the dimer of cyclohexene.

The condensation of cyclohexanol with chlorobenzene in the presence of phosphoric acid could not be accomplished even though analogous reactions with aliphatic alcohols have been reported [12]. In all cases, only the dimer and polymers of cyclohexene were obtained. These results are explained by the easy dehydration of cyclohexanol and the ability of cyclohexene to polymerize readily.

## EXPERIMENTAL

### Condensation of Chlorobenzene with Cyclohexanol in the Presence of Aluminum Chloride

The reaction was conducted in the usual apparatus with a mechanical stirrer. The results of the condensations giving the maximum yields are reported below.

13.3 g (0.1 mole) of aluminum chloride was added in small portions over a 1-hour period with efficient stirring to a mixture of 100 ml (1 mole) of chlorobenzene and 10 g (0.1 mole) of cyclohexanol. If the addition of  $AlCl_3$  was made at 20°, a violent evolution of hydrogen chloride started after the addition of all of the catalyst, which continued for 15-20 minutes; the mixture warmed up slightly with this. The mixture was allowed to stand until the following day in order to complete the reaction, and then decomposed in the usual manner. In the case of the reaction at 0°, the mixture thickened after the addition of part of the aluminum chloride, and required the addition of 100 ml more of chlorobenzene. A slow evolution of hydrogen chloride started after the addition of all of the  $AlCl_3$  and continued for 2 days. During this time the mixture was kept at 0-5°. After the decomposition of the reaction mixture, the chlorobenzene layer was washed, dried, and distilled. In both cases the yield of cyclohexylchlorobenzene with b.p. 120-121° (7 mm) was identical, 16.6 g (85% of the theoretical amount). Repeat condensations with three-fold quantities of the reagents gave the same results. Increasing the reaction temperature to 50-95°, lowered the yield to 65-70%.

Cyclohexylchlorobenzene obtained at 95° had the following constants:

B.p. 121° (7 mm);  $d_4^{20}$  1.0637;  $n_D^{20}$  1.5384;  $MR_D$  57.23.  $C_{12}H_{15}Cl$ ; calculated  $MR_D$  56.67.

p-Chlorobenzoic acid with m.p. 230° was obtained by oxidation with nitric acid ( $d$  1.111) in a sealed tube at 130-150° for 10 hours. After one recrystallization from water, the melting point rose to 238° (uncorr.). p-Chlorobenzoic acid melts at 242° according to the literature.

Cyclohexylchlorobenzene obtained at 20° had the following constants:

B.p. 121° (7 mm);  $d_4^{20}$  1.0688;  $n_D^{20}$  1.5403;  $MR_D$  57.12; calculated  $MR_D$  56.67. Found %: Cl 18.37.  $C_{12}H_{15}Cl$ . Calculated %: Cl 18.25.

Oxidation with nitric acid gave a product melting at 156-180°. Fractional crystallization gave p-chlorobenzoic acid, m.p. 238°, and crystals, melting at 140-160°, from which no individual substance could be isolated.

Dehydrogenation. The calculated amount of bromine was added dropwise to cyclohexylchlorobenzene heated to 160° in a three-neck flask with a thermometer, dropping funnel, and a reflux condenser. After the addition of all of the bromine, the heating was continued for several hours, the mixture allowed to stand until the evolution of hydrogen bromide stopped, and distilled. The following fractions were obtained: I, b.p. 267-270°; II, 274-276°; III, 280-283°. p-Chlorodiphenyl with m.p. 74° (from ligroin) was isolated from the second and third fraction upon cooling. The liquid fraction distilled at 267-270°. It corresponded to o-chlorodiphenyl according to boiling point.

Nitration [8] of cyclohexylchlorobenzene gave an oil which partially crystallized. Pure 4-chloro-2,6-dinitrocyclohexylbenzene with m.p. 92° was obtained upon recrystallization from alcohol.

Cyclohexylchlorobenzene obtained at 0° had the following constants:

B.p. 120° (7 mm);  $d_4^{20}$  1.0691;  $n_D^{20}$  1.5402;  $MR_D$  57.10.  $C_{12}H_{15}Cl$ ; calculated  $MR_D$  56.67.

Oxidation with dilute nitric acid gave a mixture of o- and p-chlorobenzoic acids which were separated by

extraction with hot water and fractional crystallization with water: p-chlorobenzoic acid with m.p. 258° composed approximately 2/3 of the total amount of the acids, while o-chlorobenzoic acid with m.p. 142°, about 1/3.

#### Condensation of Chlorobenzene with Cyclohexene in the Presence of Aluminum Chloride

The reaction was conducted with mechanical stirring. The order of addition of the reagents was always the same, cyclohexene was added to a mixture of chlorobenzene and  $AlCl_3$ . The amount of  $AlCl_3$  was varied from 0.4 to 1.0 mole per mole of cyclohexene; the chlorobenzene was always taken in ten-fold excess. The reaction temperature was varied from 20-40°. The yield of the fraction with b.p. 120-125° (7 mm) was 17-26% of the theoretical amount. In addition, considerable amounts of high boiling fractions was obtained. All of the products decolorized a solution of potassium permanganate and bromine water.

#### Condensation of Chlorobenzene with Cyclohexanol in the Presence of Phosphoric Acid

The reaction was conducted in a three-necked flask with a reflux condenser and mechanical stirrer. The phosphoric acid (d 1.86) was prepared by evaporating commercial acid in a platinum dish. The reaction was conducted under various conditions. The amount of chlorobenzene was varied from 5 to 10 moles, and the amount of phosphoric acid from 2 to 10 moles per mole of cyclohexanol. The temperature was varied from 55 to 120°, and the heating time from 1 to 10 hours. In spite of all of the variations in conditions, the reaction either did not occur, or cyclohexene with b.p. 79-82°, its dimer with b.p. 60-63° (4 mm), and polymers with b.p. 63-150° (4 mm) were obtained as reaction products. The reaction products gave a positive reaction for a double bond and a negative one for halogen.

#### SUMMARY

1. The condensation of chlorobenzene with cyclohexanol was studied and conditions which gave yields of cyclohexylchlorobenzene of up to 85% of theory were found.
2. It was shown that p-cyclohexylchlorobenzene was formed upon conducting the condensation with heating, whereas at 0-20°, a mixture of o- and p-cyclohexylchlorobenzene was obtained with the latter predominating.
3. The condensation of chlorobenzene with cyclohexanol in the presence of phosphoric acid could not be accomplished. The phosphoric acid behaved as a dehydrating and polymerizing agent.

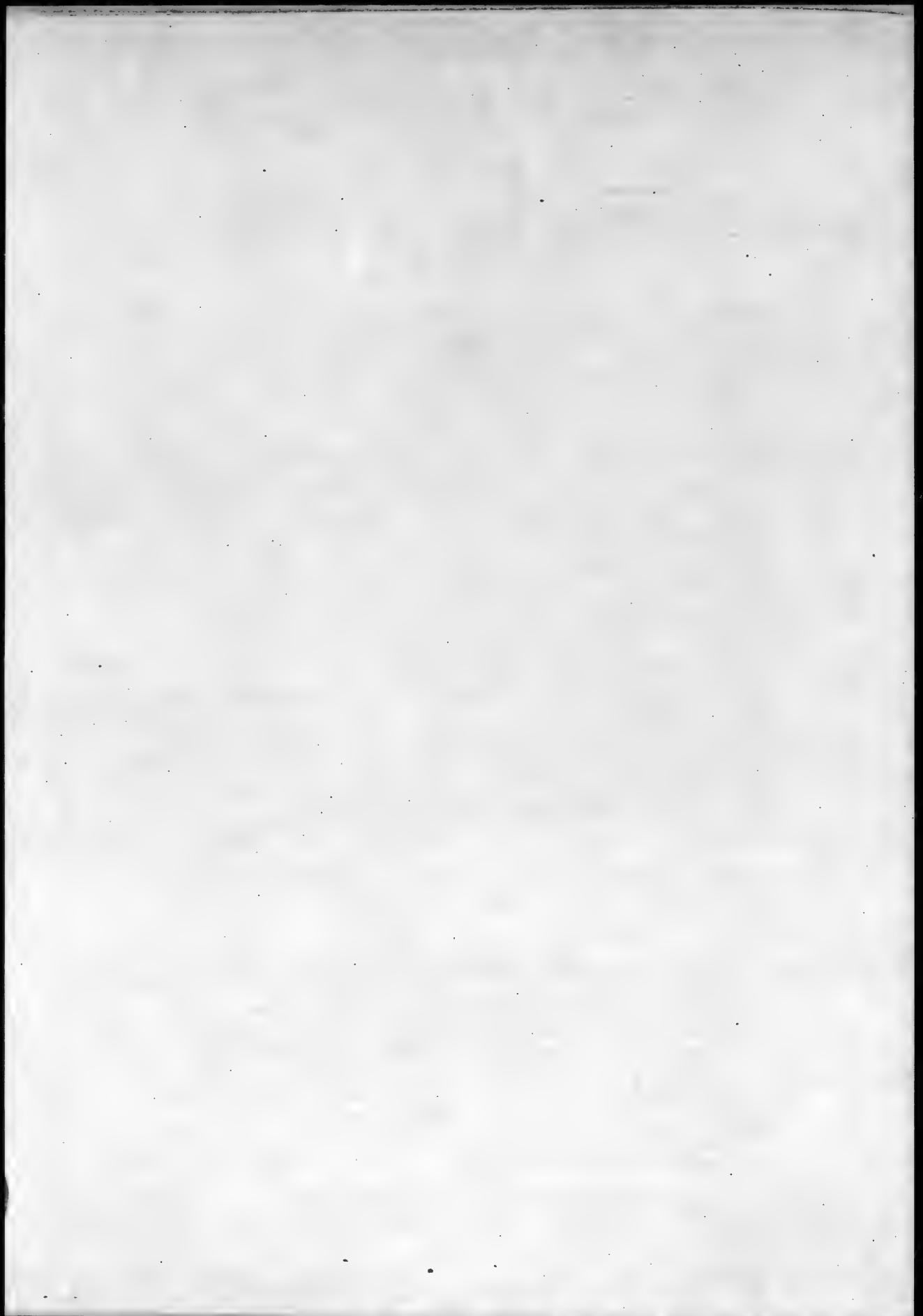
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Received December 15, 1952.

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\* See Consultants Bureau English Translation, page 1015.



# TRANSEETHERIFICATION OF DIALKYLAMINOMETHYLALKYL ETHERS

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Dialkylaminomethylalkyl ethers of the general formula  $\text{R}_2\text{NCH}_2\text{OR}$  (I) are characterized by increased reactivity, and are separated in this way from simple ethers. This is especially graphically illustrated by the reaction of (I) with organo-magnesium compounds [1].

The increased reactivity of (I) can be explained by the tendency of the C-O in these compounds to polarize as a result of which a center of electrophilic activity arises at the carbon atom of the methylene group which facilitates nucleophilic substitution.

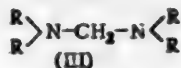
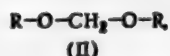
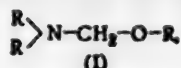
The formation of  $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{Cl} \cdot 8\text{H}_2\text{O}$ , isolated by Stewart and Bradley [2] by the neutralization of N-diethylaminomethylisobutyl ether with hydrochloric acid, and the formation of various dialkylaminomethyl derivatives with the participation of (I), reported by a series of authors [3-5], can be assigned to this type of reaction.

MacLeod and Robinson [3] obtained, by the action of diethylaminomethylethyl ether upon acetophenone and 2,4-dinitrotoluene,  $\beta$ -diethylaminopropiophenone and 2,4-dinitro- $\beta$ -diethylaminoethylbenzene, respectively, which they characterized as the chloroplatinates. Heou-Feo-Tseou and Chang-Tsing-Yang [4] obtained the piperidinomethyl derivatives by the action of piperidinomethylethyl ether on naphthol, naphthylamines, cresols, and several other substituted phenols. Burckhalter and co-workers [5] used (I) for the preparation of dialkylaminomethylphenols.

The ease with which these reactions proceeded led to the suggestion that (I) is capable of reacting with other nucleophilic reagents.

The presence of the group  $\text{>N-CH}_2\text{-O-}$  in (I) makes it possible to regard them not only as ethers, but also as the nitrogen analogs of formals, monoaminoformals. Such a view has been given more than once for compounds similar in structure. The structural analogy between acetals and bis-(dialkylamino)methylenes, on one hand [6], and acetals and bis-(stearyl-amido)methylene, on the other [7] has been pointed out.

Upon comparing (I) with formulas (II) and bis-(dialkylamino)methylenes (III), an undoubted similarity in their structures is apparent.



This resemblance is not limited to the formal formula alone. It is known that (I), as well as (II) are readily hydrolyzed in aqueous solutions by the action of acids and possess stability to alkalis. However, other reactions reported for formals were not applied to dialkylaminomethylalkyl ethers.

One of these reactions which has been more thoroughly studied for formals is the alcoholysis reaction, which can be regarded as a nucleophilic substitution at the carbon atom of the methylene group.

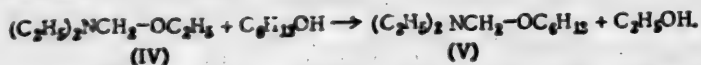
Delépine [8] obtained diamylformal as one of the reaction products by heating methylal with amyl alcohol in the presence of catalytic amounts of hydrochloric acid. Mikhitoryan [9] found that the lighter alkoxyl groups were displaced from the acetals during the reaction of methylacetal or butyraldehyde acetal with pentaerythritol in the presence of p-toluenesulfonic acid.

Kursanov, Setkina, and Rodionov [10] report on the possibility of alkoxyl radicals of formals to be exchanged by heavier ones on heating them with alcohols in the absence of catalysts.

Based upon the structural analogy of formals to dialkylamino methylalkyl ethers and the ability of these and others to substitute nucleophilically, it was suggested that the alcohols reaction would proceed with dialkylamino methylalkyl ethers.

This suggestion was confirmed experimentally [11]. Upon heating diethylaminomethylethyl ether (IV) with hexy

alcohol at 130-135° under conditions of simultaneous removal of the ethyl alcohol formed, diethylaminomethylhexylether (V) was obtained in a 76% yield:



This same alcoholysis reaction with high yields (up to 80%) proceeded with other primary alcohols of various structure: n-butyl, isobutyl, n-decyl, benzyl, cinnamyl, as well as with butylglycol and phenylglycol. In addition to primary alcohols, the alcoholysis reaction was effected with secondary alcohols: isobutyl alcohol and cyclohexanol.

As it was expected experiments conducted with tertiary alcohols methylethylisooamylcarbinol and triphenylcarbinol, did not lead to the formation of dialkylaminomethylalkyl ethers containing a tertiary alcohol residue, which agrees with the unusual characteristics of the hydroxyl found at the tertiary carbon atom [12]. Upon effecting this reaction under conditions reported in experiments with primary and secondary alcohols, the decomposition of (IV) occurred with the formation of ethyl alcohol, and a large part of the starting tertiary alcohol was recovered. The alcoholysis was also effected with diisobutylaminomethyl ethyl (VI) by the reaction of the latter with n-decyl alcohol.

A large part of the ethers prepared by this method were newly synthesized by the authors. Several of these were identified by means of ethers obtained by the reaction of dialkylamine, paraformaldehyde, and the corresponding alcohol.

Another interesting reaction is the ability of mixed formal to become symmetrical (exchange of alkoxy groups) under the influence of catalyst or with increased temperatures

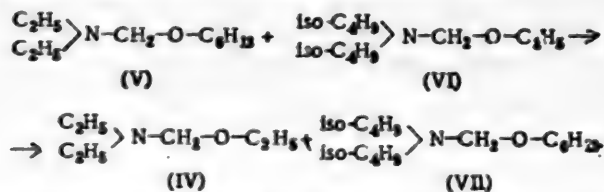
Shostakovsky and Gershstein [13] observed the formation of symmetrical acetals during the distillation of mixed ones.

Kursanov, Setkina, and Rodionov [10] obtained two symmetrical acetals in addition to the asymmetrical ones by the reaction of quaternary ammonium salts with various alcohols, which formed as a result of symmetrization of the initially formed asymmetrical acetals.

Prilezhneva, Shapiro, and Shostakovsky [14] showed the ability of  $\alpha, \beta$ -dialkoxydiethylsulfides, having the structure of monoacetals  $(CH_3-CH \begin{smallmatrix} SCH_2CH_2OR \\ OR \end{smallmatrix})$ , to disproportionate with the formation of equimolecular amounts of dialkylacetals and dialkoxydiethylmercaptals.

It also could have been supposed that dialkylaminomethylalkyl ethers (I) would possess the ability of interchanging alkoxy groups. It was considered that experimental proof of transesterification would be obtained by choosing (I) so that one of the two newly formed ethers would have considerably lower boiling point than the other, and could for this reason be removed from the sphere of the reaction. This property would enable a maximum shift of the reaction in the desired direction.

Thus, for example, the following two new ethers, must be formed by the interaction of diethylaminomethylhexyl ether (V) with diisobutylaminomethylethyl ether (VI): diethylaminomethylethyl (IV) with b.p. 132°, and the considerably higher boiling diisobutylaminomethylhexyl ether (VII):



Upon effecting this reaction, it was found that the temperature of the reaction had to be raised to 170-180° in order to distill the readily distilling transesterification product (which considerably exceeded the temperature of the mixture during the alcoholysis reaction). In addition, the temperature of the distilling liquid was much lower than the boiling point of the expected ether (IV). An investigation of the lower-boiling distillate obtained showed that ethyl alcohol was the main component part; only very small amounts of ether (IV) were contained in it. The second expected ether was isolated with a yield of 52.4% upon vacuum distillation of the reaction mixture.

Analogous results were obtained upon the transesterification of other dialkylaminomethylalkyl ethers. Methyl or ethyl alcohol was the main component of the lower boiling distillate upon the interaction of diisobutyl-



aminomethylethyl ether (VI) and diethylaminomethylbutylglycol ether, diethylaminomethyl-n-decyl ether and hexamethyleneiminomethylmethyl ether, as well as diethylaminomethylphenylglycol ether and hexamethyleneiminomethylmethyl ether.

The expected low boiling diethylmethylmethyl ether (b.p. 115°) and (IV) (b.p. 132°) were found in very small amounts. On the other hand, the higher boiling ethers, hexamethyleneiminomethylphenylglycol, hexamethyleneiminomethyldecyl, and diisobutylaminomethylbutylglycol ethers were isolated in yields of 80.7, 61.4 and 46% respectively. The presence of methyl and ethyl alcohol in the reaction products was unexpected and indicated the possible decomposition of diethylaminomethylethyl and diethylaminomethylmethyl ethers at the temperature conditions chosen for the reaction.

For this reason, the thermal stability of (IV) was investigated at the temperatures corresponding to those in the reaction.

On heating (IV) in a sealed tube to 184° (in aniline vapors) for 12 hours, a dark tarry liquid was obtained which differed in outer appearance from the starting ether. Ethyl alcohol and bis(diethylamino)methylene were identified in the reaction products by means of fractional distillation. (IV) was not isolated.

In an analogous manner it was shown that diethylaminomethylhexyl ether (V) was subjected to decomposition to a certain degree by heating for 3 hours at 170-186° with the formation of diethylamine, hexyl alcohol, and nitrogen-containing substances.

At the present time, no sort of scheme can be suggested for the thermal decomposition of dialkylaminomethyl alkyl ethers which lead to the formation of alcohols (compare [13]).

These experiments placed in doubt the results obtained on the transesterification of the ethers (I) since the formation of diisobutylaminomethylhexyl, hexamethyleneiminomethylphenylglycol, hexamethyleneiminomethyldecyl, and diisobutylaminomethylbutylglycol ethers could have occurred as a result of a series of other transformations caused by the different thermal stabilities of ether containing lighter and heavier alkoxyl residues.

In order to prove more exactly the course of the transesterification reaction of the ethers (I), experiments were conducted in order to determine the temperature conditions at which the thermal decomposition of (IV) did not occur, or occurred to the minimum degree.

It was found that only 1% of ethyl alcohol was formed after heating (IV) for 75 hours in a sealed tube at 132° (in vapors of chlorobenzene). The remaining product was, judging by the nitrogen content and refraction, unchanged (IV). After determination of the relative stability of (IV) at 132°, the transesterification experiment of (V) and (VI) was repeated under these conditions: the investigation of the reaction products was effected by vacuum distillation at temperatures also not greater than 132° in the reaction. Ethyl alcohol was not detected in this experiment. As a result of the reaction (IV) was obtained with a yield of 28.6% and (VII) with a yield of 22.7% of the theoretical.

Therefore, it was shown that alkoxyl group interchange reaction between various dialkylaminomethylalkyl ethers truly occurred.

## EXPERIMENTAL

The alcoholysis of the dialkylaminomethylalkyl ethers was conducted in a four-necked flask with a mechanical stirrer, dropping funnel, out-going condenser, and thermometers which showed the temperature of the reaction mixture and the distilling vapors. A mixture of the alcohol and some dialkylaminomethylalkyl ether was placed into the flask, and the heating of the reaction mixture was begun. The indication of the start of the reaction was the formation of a distillate of ethyl (or methyl) alcohol. The starting temperature of the alcoholysis reaction differed in relation to the starting substances used. In order to avoid side processes, the rest of (I) was gradually added at this temperature. After the addition of (I), the temperature of the reaction mixture was raised to 140-150° and was kept at this temperature until the distillation of the lower-boiling alcohol stopped completely.

The alcoholysis of diethylaminomethylethyl ether with n-hexyl alcohol is given below as a typical experimental report.

- The alcoholysis of diisobutylaminomethylethyl ether with decyl alcohol occurred at a higher temperature.

# Alcoholysis of Dialkylaminomethylalkyl Ethers (D)

Expt. No.	Starting alcohol	Structure of ether obtained	Dialkylaminomethylalkyl ether					
			Yield (%)	Boiling point (°C)	$d_4^{20}$	$n_D^{20}$	MR <sub>D</sub>	
							found	calculated
1	N-Butyl alcohol	$(C_2H_5)_2NCH_2OC_4H_9$	69.59	172-174				
2	Isobutyl alcohol	$(C_2H_5)_2NCH_2OC_4H_9^{iso}$	72.5	163-165				
3	N-Decyl alcohol	$(C_2H_5)_2NCH_2OC_{10}H_{21}^*$	32.51	146-147 at 12 mm				
4	Benzyl alcohol	$(C_2H_5)_2NCH_2OCH_2C_6H_5^*$	66.1	122-124 at 15 mm	0.9359	1.4938	60.10	59.75
5	Butylglycol	$(C_2H_5)_2NCH_2OCH_2CH_2OC_4H_9^*$	71.91	111 at 13 mm	0.8641	1.4271	60.42	60.38
6	Phenylglycol	$(C_2H_5)_2NCH_2OCH_2CH_2OC_6H_5^*$	61.65	142-146 at 10 mm	0.9981	1.4969	65.39	66.01
7	Cinnamyl alcohol	$(C_2H_5)_2NCH_2OCH_2CH:CHC_6H_5^*$	78.61	149-152 at 9 mm	0.9562	1.5260	70.40	68.52
8	Cyclohexanol	$(C_2H_5)_2NCH_2OCH(CH_2-CH_2)_2CH_3^*$	70.15	93-94 at 10 mm	0.8839	1.4493	56.26	56.54
9	Isocetyl alcohol	$(C_2H_5)_2NCH_2OC_{17}H_{35}^{iso}$	84.01	111 at 10 mm	0.8230	1.4293	67.51	67.97
10	N-Decyl alcohol	$iso-(C_4H_9)_2NCH_2OC_{10}H_{21}^*$	72.41	160-161 at 7 mm	0.8238	1.4330	94.50	95.68

Notes. Literature data for ether of experiment 1: b.p. 172-173° at 756 mm; for ether experiment 2: b.p. 165° at 760 mm. Ethers of experiments 7 and 9 were also obtained by the reaction of diethylamine, paraformaldehyde, and the corresponding alcohol; b.p. 152 at 10 mm and 111-112 at 10 mm;  $n_D^{20}$  1.5260 and 1.4292, respectively.

## Diethylaminomethyl-N-hexyl Ether (V)

a) 51 g of n-hexyl alcohol (b.p. 157-158°), 15 g of freshly distilled diethylaminomethylethyl ether (IV) (b.p. 132-134°) were placed into a flask, and the mixture was heated until the appearance of an ethyl alcohol distillate (130°). 57 g more of (IV) was added at this temperature at such a rate that the temperature of the distilling vapors did not exceed 78-80° (in order to avoid the distillation of (IV) with the vapors of the ethyl alcohol). At the end of the addition of (IV), the mixture was heated within 30 minutes up to 145° and kept at this temperature until the distillation of ethyl alcohol stopped (about 2 hours). 16.2 g of a distillate was obtained which consisted of ethyl alcohol with a small contamination of a nitrogen-containing compound (nitrogen content 0.9%). (V) was isolated after fractional distillation of the reaction mixture (71 g; yield 76%).

B.p. 90-91° at 10 mm;  $d_4^{20}$  0.8201;  $n_D^{20}$  1.4260; MR<sub>D</sub> 58.53; calculated 58.74.

3.428, 3.740 mg substance: 8.822, 9.656 mg CO<sub>2</sub>; 4.110, 4.424 mg H<sub>2</sub>O. 0.2415, 0.2346 g substance: 13.0, 12.84 ml 0.1N HCl. Found %: C 70.23, 70.46; H 13.41, 13.24; N 7.54, 7.67. C<sub>11</sub>H<sub>25</sub>ON. Calculated %: C 70.53; H 13.45; N 7.48.

The diethylaminomethyl-n-hexyl ether (V) obtained by the reaction of diethylamine, paraformaldehyde, and n-hexyl alcohol, had the following constants: b.p. 91-92° at 10 mm;  $d_4^{20}$  0.8205;  $n_D^{20}$  1.4259.

b) 20.5 g of diethylaminomethylmethyl ether (b.p. 114-115°) was added to a mixture of 20.4 g of n-hexylalcohol and 5.2 g of the former at 130-135° over a period of 1 hour. The reaction mixture was then heated for 1 hour and 30 minutes at 140° until the distillation of methyl alcohol stopped. The temperature of the distilling vapors was 65-66° (weight of the distillate 5.75 g; nitrogen content 1.55%). Diethylaminomethyl-n-hexyl ether (28.35 g; yield, 75.8%) with b.p. 92° at 10 mm was isolated by fractional distillation of the reaction mixture.

\* Ethers designated by a star are new compounds.

Alcoholysis of Dialkylaminomethylalkyl Ethers (I) - (continued)

Dialkylaminomethylalkyl ether					
Elementary analysis					
Found			Calculated		
C	H	N	C	H	N
67.67, 67.92	13.15, 12.91	8.73, 8.73	67.87	13.29	8.79
67.54, 67.68	13.21, 13.01	8.91, 8.98	67.97	13.29	8.79
		5.51, 5.48			5.75
74.26, 74.09	10.00, 9.87	7.06, 7.04	74.56	9.91	7.23
64.71, 64.91	12.04, 12.27	7.15, 7.12	64.98	12.39	6.89
70.28, 70.36	9.15, 9.36	6.30, 6.24	69.91	9.48	6.27
77.08, 77.00	9.32, 9.63	6.32, 6.33	76.68	9.66	6.39
71.31, 71.35	12.54, 12.38	7.57, 7.56	71.29	12.51	7.56
72.40, 72.27	13.46, 13.63	6.42, 6.47	72.49	13.57	6.53
76.30, 76.13	13.54, 13.45	4.50, 4.48	76.18	13.80	4.68

The experiments on the alcoholysis reaction of diethylaminomethylethyl ether with alcohols of various structure (experiments 1-9) are given in the table; experiment 10 was conducted with diisobutylaminomethyl ether.

Transesterification of Diethylaminomethyl-n-hexyl Ether (V) and Diisobutylaminomethyl Ethyl Ether (VI)

a) Transesterification at 175-200°

A mixture consisting of 33.3 g of (V) and 10 g of (VI) was heated until the appearance of a distillate (176-174°), and 25.7 g more of (VI) was added at this temperature over a one hour period. At the end of the addition of (VI), the temperature of the reaction mixture was raised to 200° and kept there for 1 hour until the distillation stopped. The temperature of the distilling vapors was 64-72°. The following were isolated upon the redistillation of the distillate obtained (15.3 g) through a laboratory rectification column: 1) ethyl alcohol (7.1 g), b.p. 77-78°; it was identified as the nitro-

benzoate with m.p. 56-56.5° from methyl alcohol; 2) diethylaminomethylethyl ether (IV) (3.7 g).

B.p. 132-134°;  $d_4^{20}$  0.8090;  $n_D^{20}$  1.4110;  $MR_D$  40.24; calculated 40.26.

0.1862, 0.1739 g substance: 14.05, 13.29 ml 0.1N HCl. Found %: N 10.63, 10.71.  $C_7H_{15}ON$ . Calculated %: N 10.68.

The reaction mixture was a dark-colored, lively liquid in external appearance, from which diisobutylaminomethylhexyl ether (VII) (22.7 g; yield, 52.46%) was obtained upon two fractional vacuum distillations.

B.p. 132.4-133.6° at 12 mm;  $d_4^{20}$  0.8188;  $n_D^{20}$  1.4363;  $MR_D$  77.77; calculated 77.21

3.363, 3.526 mg substance: 9.150, 9.580 mg  $CO_2$ ; 3.984, 4.240 mg  $H_2O$ . 0.3066, 0.3197 g substance: 13.22, 14.02 ml 0.1N HCl. Found %: C 74.24, 74.16; H 13.27, 13.46; N 6.04, 6.14.  $C_{12}H_{25}ON$ . Calculated %: C 74.01; H 13.63; N 5.76.

b) Transesterification at 132°. A mixture of 20 g of (V) and 20 g of (VI) (equimolecular amounts) was heated in a sealed tube for 75 hours in the vapors of boiling benzene. No pressure was detected upon opening the tube. In contrast to experiment (a), the reaction mixture yellowed slightly. Fractional distillation of the mixture was effected at a temperature not higher than 132° in n.e. mass.

(IV) (4 g, yield 28.6%) was isolated from the first fraction which was collected at 130-130° after redistillation.

$d_4^{20}$  0.8088;  $n_D^{20}$  1.4069;  $MR_D$  39.93; calculated 40.26.

0.1911, 0.2350 g substance: 6.1-6.79 ml 0.1N HCl. Found %: N 11.1, 11.2.  $C_7H_{15}ON$ . Calculated %: N 10.68.

Then several intermediate fractions were isolated which were a mixture of starting and final reaction products according to the nitrogen content and boiling point. The last fraction was (VII) (5.9 g; yield 22.7%).

B.p. 130-133° at 12 mm;  $d_4^{20}$  0.8187;  $n_D^{20}$  1.4310;  $MR_D$  76.97; calculated 77.2°

0.1501, 0.1519 g substance: 6.31, 6.45 ml 0.1N HCl. Found %: N 5.89, 5.95.  $C_{12}H_{25}ON$ . Calculated %: N 5.76.

Diisobutylaminomethylhexyl ether (VII), obtained by the reaction of n-hexyl alcohol, diisobutylamine, and paraformaldehyde, had the following constants:

B.p. 133–134° at 12 mm;  $d_4^{20}$  0.8178;  $n_D^{20}$  1.4360;  $M_R^D$  77.62.

### SUMMARY

1. The analogy between the structures of dialkylaminomethylalkyl ethers (I) and formals was pointed out and it was shown that a substitution of the lighter alkoxy residue by a heavier one occurred by the action of primary and secondary alcohols upon (I).

2. The ability of dialkylaminomethylalkyl ethers to undergo alkoxy radical exchange reactions was shown.

3. A series of new dialkylaminomethylalkyl ethers was synthesized.

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Received April 25, 1953

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\*See Consultants Bureau Translation, page 459.

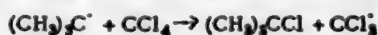
# REACTION OF CARBON TETRACHLORIDE WITH ETHYL ALCOHOL

G. A. Razuvaev and Yu. A. Sorokin

The substitution of chlorine by hydrogen during the reaction of  $\text{CCl}_4$  with organic compounds has been little studied as yet. Such reactions proceed mainly in the presence of peroxides and have a chain character. Thus, in the case of the addition of  $\text{CCl}_4$ , initiated by acetyl peroxide or benzoyl peroxide, to olefins, in addition to heat polymerization, a concurrent process occurs which breaks the chain by means of the removal of a hydrogen from the  $\alpha$ -carbon atom by a  $\text{CCl}_3$  radical with the formation of a poorly active allyl type radical which is incapable of prolonging the chain, and chloroform [1].



The substitution of chlorine by hydrogen also occurs on the heating of saturated hydrocarbons with  $\text{CCl}_4$  in the presence of benzoyl peroxide or tertiary butyl peroxide. The hydrogen of a tertiary carbon atom is the most active, and then that of the secondary [2].



However, during the reaction of  $\text{CCl}_4$  with polychlorides (tetrachloroethane and trichloroethane) at higher temperature (400°), the latter are only dehydrogenated by atomic chlorine, while the  $\text{CCl}_3$  radicals dimerize into hexachloroethane [3].



The formation of chloroform occurs during the heating of  $\text{CCl}_4$  with aldehydes which are transformed into acid chlorides. The reaction proceeds in the presence of peroxides. The radicals obtained by the decomposition of peroxides, remove hydrogen from the aldehyde to give acyl radicals which react further with  $\text{CCl}_4$ . Therefore, a chain process is created [4].



A reaction occurs between  $\text{CCl}_4$  and methanol in the absence of peroxides on heating the components to 200° with the formation of chloroform. This corresponds to the following summary equation:



Then secondary processes proceed with the formation of methyl chloride as a result of the reaction of hydrogen chloride with methanol, and methylal, because of the reaction of formaldehyde with methanol in the presence of HCl.

The direction of the reaction changes by the ultraviolet illumination of a mixture of  $\text{CCl}_4$  and methanol: the  $\text{CCl}_3$  radicals dimerize to hexachloroethane; chloroform is not found in the reaction products. The process occurs according to the summary equation [5]:



It is of interest to continue the investigation of the reaction of  $\text{CCl}_4$  with alcohols. Ethyl alcohol was used for this purpose, and it reacted with  $\text{CCl}_4$  in an analogous manner. The separation of the reaction mixture into two layers occurred during the thermal reaction after heating the components to 200°. The aqueous layer contained alcohol and HCl. The non-aqueous layer consisted of a mixture of chloroform,



ethyl chloride, ethyl ether, paraldehyde, and unreacted  $\text{CCl}_4$  and alcohol.

On the basis of the products obtained, it could be concluded that the primary process is the dehydrogenation of alcohol, which occurs according to the equation:



Then secondary processes proceed: ethyl chloride is formed by the reaction of  $\text{HCl}$  with alcohol which then gives ethyl ether with alcohol. Acetaldehyde polymerizes into paraldehyde.

The course of the photoreaction of  $\text{CCl}_4$  with ethyl alcohol is different: the dehydrogenation of alcohol also occurs, but only by the action of chlorine. The  $\text{CCl}_3$  radicals do not remove a hydrogen, but dimerize into hexachloroethane. The summary reaction has the following form:



The hydrogen chloride does not react with the alcohol under the given conditions, and the above mentioned side reactions do not occur.

In order to prove the different courses of the thermo- and the photoreactions, the reaction between hexachloroethane and alcohol was studied. It could be supposed that hexachloroethane, dissociating into two  $\text{CCl}_3$  radicals, would give chloroform on heating with alcohol. In this case, it could be considered that courses of the photo- and thermo- action would be identical in the initial stage. However, the experiments conducted showed that the dehydrogenation of alcohol occurred by means of two cleaving chlorine atoms during the heating of alcohol with hexachloroethane. Hexachloroethane is converted into perchloroethylene. The primary process can be represented as follows:



Then follow the processes given above, the formation of ethyl chloride, ether, and paraldehyde. The reaction occurs at higher temperatures and is accompanied by a considerable tarring.

The thermal reaction between  $\text{CCl}_4$  and alcohol is accelerated by the addition of a small amount of mercuric chloride, which is transformed into mercurous chloride. In the end, the same products are obtained as without the addition of mercuric chloride.

## EXPERIMENTAL

Thermal reaction of  $\text{CCl}_4$  with ethyl alcohol. 16 ml of  $\text{CCl}_4$  (0.17 mole) and 20 ml of 98% ethyl alcohol (0.34 mole) were heated in a sealed tube for 15 hours at  $200^\circ$ . The reaction mixture separated into two layers, an aqueous (upper) and a non-aqueous. Products from two experiments were used for the investigation. The tubes, cooled by a mixture of ice and salt, were opened and their contents processed. 8.4 g of an aqueous and 74.2 g of a non-aqueous part were obtained. The aqueous part was a colorless liquid with a pleasant odor, which yellowed upon prolonged standing; it had an acid reaction to Congo, the non-aqueous part was a mobile, dark raspberry colored liquid with a specific ethereal odor. 7.9 g was washed out by three treatments with small portions of ice water. The wash waters were combined with the aqueous portion, the amount of  $\text{HCl}$  determined by titration (0.06 g), and the free acetaldehyde precipitated with dimedon (0.8 g; melting point of the derivative,  $140^\circ$ ; no depression in mixed melting point). The non-aqueous part was separated into two portions by distillation: I, 52.7 g, up to  $68^\circ$ ; II, 13.3 g, residue.

The condensate was dried and fractionated through an effective distilling column. A trap cooled with a mixture of dry ice and toluene was connected to the receiver of the column. The following fractions were obtained: 1—6.4 g to  $25^\circ$  (in trap); 2—3.8 g,  $25.0-41.5^\circ$ ; 3—7.5 g,  $41.5-62.2^\circ$ ; 4—30.8 g,  $62.0-77.0^\circ$ ; residue 2.1 g.

Fraction 1 was ethyl chloride containing traces of acetaldehyde. The ethyl chloride was identified by conversion into ethyl mercuric chloride with m.p.  $191.5^\circ$ . The acetaldehyde, washed out with ice water, was identified as the dimedon derivative.

Fraction 2 was distilled, whereby 3.1 g of ethyl ether was collected at  $34.1-35.0^\circ$ .

6.7 g of chloroform boiling at  $59.2-62.0^\circ$ ;  $d_4^{20}$  1.481;  $n_D^{20}$  1.440; MR 21.26; calculated 21.40, was isolated from fraction 3 after a supplementary drying with calcium chloride and distillation over  $\text{P}_2\text{O}_5$ .

Fraction 4 was distilled over  $\text{P}_2\text{O}_5$ . 29.6 g of a condensate boiling at  $65.6-77.0^\circ$  was obtained, a mixture containing mainly  $\text{CCl}_4$ . The residue (13.5 g) was distilled, first at atmospheric pressure, and then in vacuum.

The following fractions were obtained: 1 - 7.5 g, 68-98°; 2 - 3.2 g, 65-85° (at 18 mm), residue, 2.8 g, a solid glass-like, dark brown mass, readily soluble in acetone. Fraction 1 was a mixture of paraldehyde and  $\text{CCl}_4$ , which was proved by the preparation of acetaldehyde-2,4-dinitrophenylhydrazone with m.p. 167.5°. Fraction 2 was a straw-yellow viscous liquid which decolorized bromine water; it was not investigated further.

The reaction of  $\text{CCl}_4$  with alcohol in the presence of mercuric chloride was effected with the same amounts of components. 1 g of mercuric chloride was used for each tube. The heating time (at 200°) was 15 hours. The reaction mixture also separated into two layers, and a friable precipitate of mercurous chloride crystals formed on the bottom of the tube (98% based on the mercuric chloride used). 0.1 g of HCl was found by the combined titration of the aqueous part and the wash water (from both tubes). Acetaldehyde was identified as the 2,4-dinitrophenylhydrazone (m.p. 147°). The subsequent processing of the non-aqueous part was effected in the same manner as in the previous experiments. 7.2 g of chloroform (b.p. 59.2-61.4°;  $d_4^{20}$  1.478;  $n_D^{20}$  1.450; MR 21.60, calculated 21.40), 5 g of ethyl chloride (identified as in the previous manner), and 3.5 g of ethyl ether (34.0-34.4°) were obtained.

Photochemical reaction of  $\text{CCl}_4$  with ethyl alcohol. 16 ml of  $\text{CCl}_4$  and 20 ml of ethyl alcohol were illuminated in a quartz apparatus by the light of a mercury-quartz lamp for 520 hours. A trap containing alkali was fitted on a glass holder with the apparatus. The reaction mixture started to separate into two layers after approximately 56 hours. The boundary of the lower layer rose and then remained at the same level (corresponding to a volume of 10.1 ml for the lower layer). The brown colored reaction mixture was washed with water, and the aqueous layer was separated. 4.8 g of HCl was found by titration, in the trap and in the aqueous layer, which corresponded to 78.6% based on the  $\text{CCl}_4$  used for the reaction. Acetaldehyde was precipitated in the form of the dimedon derivative with m.p. 140° (0.5 g). After careful distillation of the carbon tetrachloride from the non-aqueous part, 3.1 g of hexachloroethane was isolated. The sublimed product melted at 185° (closed capillary).

Thermal reaction of hexachloroethane with ethyl alcohol. 15 g of  $\text{C}_2\text{Cl}_6$  (0.06 mole) and 30 ml of 98% ethyl alcohol (0.51 mole) were heated in a sealed tube for 24 hours at 220°. The reaction mixture tarred badly and separated into two layers. Material from two tubes was used for the investigation, which was then processed as given above. The amount of HCl (0.4 g) was determined by titration of the aqueous layer (16.5 ml) and the wash water. Acetaldehyde was identified as the 2,4-dinitrophenylhydrazone (m.p. 168°). The non-aqueous part of the reaction mixture (55.2 g) was separated from the tarry products (3.1 g) by distillation to 146°; the condensate was dried with calcium chloride, and fractionated through an effective laboratory column. The following fractions were obtained: 1 - 7.5 g, to 34° (in trap); 2 - 2.2 g, 34.0-34.6°; 3 - 20.3 g, 34.6-98.5°; 4 - 18.5 g, 98.5-145.0°; residue 3.5 g.

Fraction 1 was ethyl chloride with impurities of acetaldehyde.

Fraction 2 was ethyl ether.

Fractions 3 and 4 combined were treated with several drops of concentrated sulfuric acid with slight heating; the black aldehydic mass formed was discarded, and perchloroethylene (6 ml) was collected upon redistillation through a small effective column at 120.1-120.5°.

$d_4^{20}$  1.625;  $n_D^{20}$  1.501; MR 30.05;  $\text{C}_2\text{Cl}_6$ ; calculated 30.39.

#### SUMMARY

1. Acetaldehyde, chloroform, and HCl were obtained upon heating carbon tetrachloride with ethyl alcohol. The reaction was accompanied by the subsequent processes forming ethyl chloride, ethyl ether, paraldehyde, and other products.

2. The photoreaction between the same components proceeded in another direction. The alcohol was dehydrogenated to acetaldehyde by one chlorine atom of the  $\text{CCl}_4$  with the formation of hydrogen chloride. The  $\text{CCl}_3$  radicals were dimerized to hexachloroethane.

3. Hexachloroethane was not an intermediate product of the thermal reaction of  $\text{CCl}_4$  with alcohol, since perchloroethylene, HCl, and acetaldehyde was formed upon heating  $\text{C}_2\text{Cl}_6$  with ethanol.

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Received May 20, 1952.

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# NITRATION OF 1-PROPYLNAPHTHALENE AND 4-NITRO-1-PROPYLNAPHTHALENE; 4-AMINO-1-PROPYLNAPHTHALENE AND SEVERAL DERIVATIVES

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The nitration reaction of 1-propylnaphthalene and its nitro- and amino-derivatives was first investigated in this study. A detailed report on the method for the preparation of 1-propylnaphthalene by the hydrogenation of 1-allylnaphthalene in the presence of platinum black is given in R. Ya. Levina and coworkers' paper [1]. In addition, the hydrogenation of 1-allylnaphthalene with a nickel catalyst [2] at high pressure has been reported in the literature. This hydrocarbon was now hydrogenated in the presence of Raney nickel without the use of high pressures.

The nitration of 1-propylnaphthalene was effected with nitric acid of various concentrations, without solvent, or in glacial acetic acid solution.

The best results were obtained by nitrating with nitric acid ( $d$  1.40) without a solvent at 40°. In this case, a liquid mixture (yield 30%) was obtained after nitration, from which crystalline 4-nitro-1-propylnaphthalene could be isolated in a yield of 35%. The position of the nitro group in it was proved by oxidation with nitric acid in a sealed tube as a result of which 4-nitro-1-naphthoic acid was formed.

After the separation of the crystalline 4-nitro-1-propylnaphthalene (see the experimental section), a liquid substance with a higher boiling point remained; upon investigation, it was shown that it was a mixture of mono-nitropropylnaphthalenes.

4-Nitro-1-propylnaphthalene was converted into 4-amino-1-propylnaphthalene upon catalytic reduction with hydrogen in the presence of Raney nickel; acyl derivatives and several other compounds of interest for pharmacological investigation were obtained from this compound.

## EXPERIMENTAL

### 1-Allylnaphthalene

The preparation of 1-allylnaphthalene from naphthyl magnesium bromide and allyl bromide was reported by Fieser and Herschberg [3]; these investigators recommended the addition of the Grignard reagent to the allyl bromide, which requires a special apparatus. The order of addition of the reactant was changed.

207.2 g of 1-bromonaphthalene in 400 ml of absolute ether was added to 25 g of magnesium and heated for 2–3 hours. Upon cooling to room temperature, 100 ml of benzene and 121 g of allyl bromide in 200 ml of absolute benzene was added, and the mixture was heated for 2.5 hours more. After treatment of the reaction mixture with hydrochloric acid, the benzene ether layer was washed with water, then with a sodium hydroxide solution, once more with water, and dried with calcium chloride. After removal of the solvents, the substance remaining was vacuum distilled. 102.6 g (60% of the theoretical) of 1-allylnaphthalene with b.p. 134–135° at 11 mm was obtained.

### 1-Propylnaphthalene

A solution of 25 g of 1-allylnaphthalene in 150 ml of 96% ethyl alcohol and 5.5 g of nickel catalyst in 20 ml of ethyl alcohol was shaken in an atmosphere of hydrogen. Upon completion of the reaction, the purification of 1-propylnaphthalene was effected by the method of R. Ya. Levina and coworkers [1]. The yield of 1-propylnaphthalene with b.p. 119–120° at 17 mm was 23.5 g (93% of the theoretical). After redistillation over sodium, b.p. 134.5° at 11.5 mm;  $d^{20}_D$  1.9904;  $n^{20}_D$  1.5928.

### 4-Nitro-1-propylnaphthalene

1) 62 ml of nitric acid ( $d$  1.40) was added at 40° over one hour to 30.9 g of 1-propylnaphthalene. After the addition of the acid, the mixture was stirred for 20–30 minutes more, and then poured into water. The acidic solution was extracted with ether. The ether solution was washed with sodium carbonate solution, then with water,

and dried with calcium chloride. The ether was removed, and substance remaining was vacuum distilled. The substance came over at 159–161° at 2 mm. Yield, 31.3 g (80%). A dark tarry substance was in the residue.

After many redistillations of the substance with b.p. 159–161° at 2 mm, a substance with b.p. 143–144° at 1.5 mm was collected. Yield 14.5 g.

5.030 mg substance: 0.234 ml  $N_2$  (25.5°, 734.0 mm). 3.141 mg substance: 8.359 mg  $CO_2$ ; 1.793 mg  $H_2O$ . Found %: N 6.46; C 72.57; H 6.39.  $C_{13}H_{11}O_2N$ . Calculated %: N 6.51; C 72.54; H 6.09.

The substance with b.p. 143–144° at 1.5 mm partially crystallized several hours after distillation; it was dissolved in petroleum ether, and the solution was cooled; a solid nitropropylnaphthalene crystallized upon scratching. A substance with m.p. 33–35° was obtained after washing with cold petroleum ether on the funnel. The substance with m.p. 33–35° was vacuum distilled in order to determine its boiling point; b.p. 145.5° at 1.5 mm. For analysis, the substance with m.p. 33–35° was recrystallized from petroleum ether; a light yellow crystalline substance with m.p. 34–35° was obtained; the substance was soluble in petroleum ether, alcohol and other organic solvents.

7.385 mg substance: 0.433 ml  $N_2$  (21.0°, 732.5 mm). 0.700 mg substance: 0.381 ml  $N_2$  (18.0°, 720.0 mm). 4.481 mg substance: 1.910 mg  $CO_2$ ; 2.437 mg  $H_2O$ . Found %: N 6.56, 6.32; C 72.48; H 6.08.  $C_{13}H_{11}O_2N$ . Calculated %: N 6.51; C 72.54; H 6.09.

2) The nitration and subsequent processing of the product of the nitration of 40.9 g of 1-propylnaphthalene was effected as in the previous experiment. A substance with b.p. 164–169° at 3 mm was obtained. Yield 42.3 g (82.6%). 42.3 g of the liquid reaction product was dissolved in alcohol. Upon cooling the solution and scratching, a crystalline substance formed. After recrystallization from petroleum ether, 15.4 g (30% of the theoretical; 40% of the total mixture of nitropropylnaphthalenes) of a substance with m.p. 33–35° was obtained. The alcohol was distilled off from the mother liquor remaining after the removal of the substance which crystallized upon cooling the alcoholic solution. The substance remaining was vacuum distilled; it was separated into two fractions: 1–153–156° at 2 mm and 2–164–166° at 2 mm. No solid nitro compound could be formed upon dissolving each of the fractions in petroleum ether and cooling.

Upon investigation of all of the petroleum ether mother liquor from the two experiments, 4-nitro-1-propylnaphthalene and a liquid substance with b.p. 153–154° at 2 mm;  $n_D^{20}$  1.6170;  $d_4^{20}$  1.677, were isolated in small amounts.

10.430 mg substance: 0.600 ml  $N_2$  (25.0°, 729.5 mm). 4.299 mg substance: 11.420 mg  $CO_2$ ; 2.346 mg  $H_2O$ . Found %: N 6.33; C 72.45; H 6.10.  $C_{13}H_{11}O_2N$ . Calculated %: N 6.51; C 72.54; H 6.09.

3 g of the liquid substance with b.p. 153–154° at 2 mm and 21 ml of nitric acid (11%) were heated for 7 hours at 168–173° in a sealed tube. A substance with a constant melting point could not be isolated from the mixture of crystalline and tarry substances formed.

5.1 g of the substance with b.p. 153–154° at 2 mm, 50 ml of ethyl acetate, and 11 g of Raney nickel catalyst were shaken in an atmosphere of hydrogen. A substance with b.p. 155–156° at 3 mm was obtained at the end of the reaction and usual processing. The acetyl derivative obtained from this substance melted at 133.5–135°. No depression was found in a mixed melting point of this substance and 4-acetylamino-1-propylnaphthalene.

Oxidation of 4-nitro-1-propylnaphthalene. 2.8 g of 4-nitro-1-propylnaphthalene with m.p. 34–35° and 38 ml of nitric acid (11%) were heated for 6.5 hours at 168° and 1 hour at 168–173° in a sealed tube. 4-Nitro-1-naphthoic acid with m.p. 221.5–222.5° was isolated upon purification of the substance formed. Mixed melting point of this substance with 4-nitro-1-naphthoic acid obtained by another method (m.p. 223–223.5°) showed no depression (m.p. 222–223°).

#### 4-Amino-1-propylnaphthalene

10 g of Raney nickel catalyst was added to a solution of 10 g of 4-nitro-1-propylnaphthalene in a mixture of 50 ml of ethyl acetate and 80 ml of ethyl alcohol, and the hydrogenation was effected. At the completion of the reaction, the catalyst was filtered, and the solvent removed. The substance remaining was dissolved in ether. The ether solution was dried with potassium hydroxide. After removal of the ether, the substance was vacuum distilled. B.p. 172–175° at 8–9 mm. Yield, 6.85 g (80%). Upon redistillation, the substance distilled completely at 154.5° (3 mm).

6.449 mg substance: 3.40 ml 0.01N  $H_2SO_4$ . 5.790 mg substance: 3.00 ml 0.01N  $H_2SO_4$ . 4.596 mg substance: 14.212 mg  $CO_2$ ; 3.329 mg  $H_2O$ . Found %: N 7.38, 7.25; C 84.39; H 8.11.  $C_{12}H_{11}N$ . Calculated %: N 7.56; C 84.24; H 8.16.

\*m.p. 33–55°



4-Acetylamino-1-propylnaphthalene. 2.2 ml of acetic anhydride was added to 2.3 g of amino-propylnaphthalene in 1 ml of benzene. The crystalline substance obtained melted at 133° after two recrystallizations from aqueous alcohol; 4-acetylamino-1-propylnaphthalene dissolved in alcohol, acetone, benzene; it did not dissolve in water.

5.935 mg substance: 0.340 ml N<sub>2</sub> (28.0°, 728.0 mm). Found %: N 6.22. C<sub>15</sub>H<sub>17</sub>ON. Calculated %: N 6.16.

4-Benzoylamino-1-propylnaphthalene. 0.49 g of benzoyl chloride was added to a solution of 0.5 g of 4-amino-1-propylnaphthalene and 0.45 g of dimethylaniline on 10 ml dry benzene; a precipitate formed. A substance (0.75 g) was obtained after the usual processing which melted at 165-166° after recrystallization first from aqueous alcohol and then from benzene. The substance dissolved upon heating in benzene, dissolved readily in alcohol and acetone, and did not dissolve in water.

8.177 mg substance: 0.354 ml N<sub>2</sub> (25°, 727.0 mm). Found %: N 4.74. C<sub>20</sub>H<sub>19</sub>ON. Calculated %: N 4.84.

Ethyl ester of (1,4-propylnaphthyl)carbamic acid C<sub>3</sub>H<sub>7</sub>C<sub>10</sub>H<sub>7</sub>NHCOOC<sub>2</sub>H<sub>5</sub>. 0.45 g of ethyl chlorocarbonate was added to a solution of 0.5 g of 4-amino-1-propylnaphthalene and 0.45 g of dimethylaniline in 8 ml of absolute benzene, and heated for 3 hours at 40-50°. After the usual processing and many recrystallizations from petroleum ether, a substance with m.p. 69.5-70°, soluble in organic solvents, and insoluble in water, was obtained.

6.658 mg substance: 2.67 ml 0.1N H<sub>2</sub>SO<sub>4</sub>. Found %: N 5.58. C<sub>14</sub>H<sub>17</sub>O<sub>2</sub>N. Calculated %: N 5.45.

Isopropyl ester of (1,4-propylnaphthyl)carbamic acid C<sub>3</sub>H<sub>7</sub>C<sub>10</sub>H<sub>7</sub>NHCOOC<sub>3</sub>H<sub>7</sub>-iso. 0.7 g of isopropyl chlorocarbonate in 7 ml of absolute benzene was added to a solution of 0.75 g of 4-amino-1-propylnaphthalene and 0.7 g of dimethylaniline. The m.p. was 105.5-106.5° after recrystallization of the substance obtained from petroleum ether. Long white needles dissolving readily in organic solvents and not soluble in water were obtained.

9.240 mg substance: 0.435 ml N<sub>2</sub> (23.0°, 727.0 mm). 5.130 mg substance: 0.242 ml N<sub>2</sub> (24.5°, 728.0 mm). Found %: N 5.19, 5.01. C<sub>14</sub>H<sub>17</sub>O<sub>2</sub>N. Calculated %: N 5.16.

Methyl ester of (1,4-propylnaphthyl)carbamic acid C<sub>3</sub>H<sub>7</sub>C<sub>10</sub>H<sub>7</sub>NHCOOCH<sub>3</sub>. 0.45 g of methyl chlorocarbonate was added to a solution of 0.5 g of 4-amino-1-propylnaphthalene and 0.45 g of dimethylaniline in 8 ml of absolute benzene. The reaction procedure and processing of the substance was the same as in the previous experiments. The substance obtained melted at 67-68° after recrystallization from petroleum ether. Shiny plates readily dissolving in organic solvents and insoluble in water were obtained.

7.732 mg substance: 0.403 ml N<sub>2</sub> (25.0°, 735.0 mm). 3.089 mg substance: 8.400 mg CO<sub>2</sub>; 1.990 mg H<sub>2</sub>O. Found %: N 5.77; C 74.21; H 7.21. C<sub>13</sub>H<sub>17</sub>O<sub>2</sub>N. Calculated %: N 5.76; C 74.06; H 7.04.

1,4-Propylnaphthylamide of carbomethoxysulfanilic acid C<sub>3</sub>H<sub>7</sub>C<sub>10</sub>H<sub>7</sub>NHSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NHCOOCH<sub>3</sub>. 1.5 g of carbomethoxysulfanilic chloride was added to a solution of 1 g of 4-amino-1-propylnaphthalene in 10 ml of pyridine bases, and the solution heated on the water bath for 5 hours at 55-60°. At the end of the heating, the solution was poured into water; an oil separated which crystallized upon cooling and scratching. 1.6 g with m.p. 175-186° was obtained. M.p. 182.5-183° after two more recrystallizations from dichloroethane. A white crystalline substance, difficultly soluble in alcohol and insoluble in water.

0.1699 g substance: 0.0906 g BaSO<sub>4</sub>. 0.1752 g substance: 0.0919 g BaSO<sub>4</sub>. Found %: S 7.97, 7.78. C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>S. Calculated %: S 8.02.

C<sub>3</sub>H<sub>7</sub>C<sub>10</sub>H<sub>7</sub>NHSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>. 1,4-Propylnaphthylamide of sulfanilic acid. 0.55 g of (1-propylnaphthyl-4)amide of carbomethoxysulfanilic acid and 10 ml of a 13% solution of NaOH was heated for 2 hours. Upon cooling, the reaction mixture was acidified with dilute acetic acid. 0.4 g of a substance was obtained which melted at 175.5-176.5° after recrystallization from alcohol. The substance dissolved in alcohol and other organic solvents.

3.462 mg substance: 8.496 mg CO<sub>2</sub>; 1.701 mg H<sub>2</sub>O. 3.880 mg substance: 9.517 mg CO<sub>2</sub>; 1.980 mg H<sub>2</sub>O. Found %: C 66.97, 66.94; H 5.82, 5.71. C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub>S. Calculated %: C 67.04; H 5.92.

#### SUMMARY

1. 4-Amino-1-propylnaphthalene was isolated upon nitration of 1-propylnaphthalene; its structure was proved.
2. 4-Amino-1-propylnaphthalene, its acyl and other derivatives were obtained.

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Received April 20, 1953.

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# INVESTIGATIONS OF HYDROXYFUCHSONE DYES

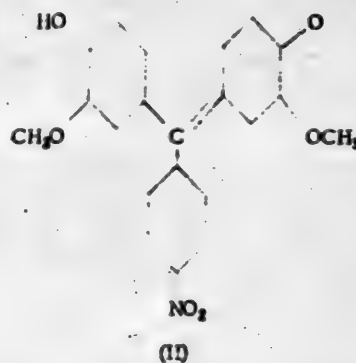
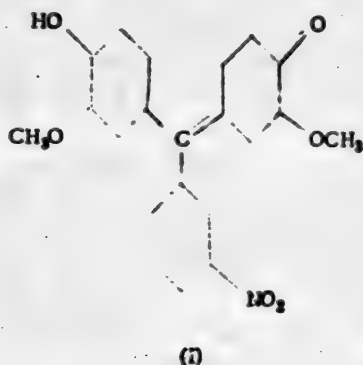
## XVII. CONDENSATION OF ISOMERIC NITROBENZALDEHYDES WITH GUAIACOL

I. S. Ioffe and B. G. Belenky

Nitro derivatives of hydroxyfuchsons have scarcely been studied. Only in one patent [1] is the preparation of 3'-nitro-3,3'-dimethoxy-4-hydroxyfuchson hydrochloride (I) reported; however, this dye was not isolated in the free state by the authors of the patent.

The condensation of isomeric o-, m-, and p-nitrobenzaldehyde with guaiacol was conducted under conditions used in the authors' laboratory [2] for the preparation of various hydroxyfuchsons which consisted of the saturation of a mixture of the aldehyde and phenol with dry hydrogen chloride, followed by allowing this mixture to stand at room temperature.

The corresponding triphenylmethane derivatives were obtained by the condensation of m-nitrobenzaldehyde and p-nitrobenzaldehyde with guaiacol from which 3'-nitro-3,3'-dimethoxy-4-hydroxyfuchson (I) and 4'-nitro-3,3'-dimethoxy-4-hydroxyfuchson (II) were obtained in the form of the hydrochlorides by oxidation with nitrous oxide in amyl acetate saturated with hydrogen chloride [2].



These dyes formed, in a manner similar to the parent substance of this group, benzaurin, hydrate forms by the hydrolysis of their salts, which firmly retained water. In order to obtain these dyes in the anhydrous forms, a method was used which was applied in the authors' laboratory [3] for the preparation of methoxyfuchson and which consisted of the heating of the hydrate form of the dye with glacial acetic acid, followed by co-distillation of the solvent and the water in vacuum. The dyes obtained crystallized readily from glacial acetic acid. The m-nitro derivative (I) was obtained in the form of orange-red crystals with m.p. 229-230° [2]. The p-nitro derivative (II) was obtained in the form of bright red crystals with m.p. 235-236°. Both dyes were soluble in mineral acids with a violet color; in alkalis they were soluble with the appearance of a blue color with a distinct greenish shade for the p-isomer.

Gold-yellow crystals with m.p. 181-182° were obtained from o-nitrobenzaldehyde upon condensation with guaiacol under the above conditions, after recrystallization from alcohol. Supposing that this substance was a usual condensation product of the triphenylmethane structure, it was oxidized in order to convert it into the corresponding fuchson dye. However, the substance remained unchanged. Analytical determination revealed that the given compound contained chlorine which was not saponified upon heating with sodium hydroxide; the substance had the composition  $C_{14}H_{11}O_3NCl$ , and therefore, it was formed as the result of the condensation of 1 molecule of o-nitrobenzaldehyde with 1 molecule of guaiacol with the simultaneous chlorination of one of the benzene rings, because of the presence of the hydrogen chloride. Such an "anomalous" behavior of o-nitrobenzaldehyde upon condensation with several phenols in the presence of hydrochloric acid has previously been mentioned in the literature.

Even in 1901, Guyot and Haller [4], desiring to prepare nitrobenzaurin, conducted the condensation of o-nitrobenzaldehyde with phenol, using hydrochloric acid as the condensing agent. However, they obtained chlorohydroxy-

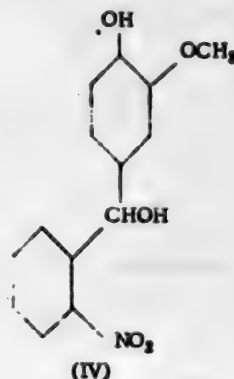
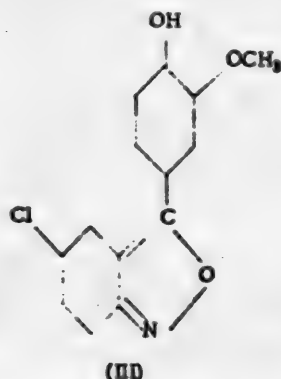
acridone instead of the desired triphenylmethane derivative, which was formed as a result of the rearrangement of the intermediately formed o-nitrodiphenylcarbinol derivative, followed by the cyclization of the acridone ring; the introduction of the chlorine, evidently, occurred during the process of the above rearrangement as a result of oxidative chlorination.

However, Zincke and Siebert [5] suggested that the substance formed during the condensation of o-nitrobenzaldehyde with phenol in the presence of hydrochloric acid was not the acridone derivative, but an anthranil. An analogously constructed compound was obtained by the condensation of o-nitrobenzaldehyde with dimethylaniline under the same conditions [6].

This conclusion was based on the fact that these condensation products of o-nitrobenzaldehyde with phenol or with dimethylaniline were readily transformed into diphenylketone derivatives upon reduction. Such a cleavage of the rings was rather likely with anthranils, and not very with acridones. The views of Zincke and co-workers were confirmed by Bamberger [7]. He showed that the products of the condensation of o-nitrobenzaldehyde with phenols in the presence of hydrochloric acid, were converted into amino compounds by reduction with zinc in acidic medium, which could be easily detected by diazotization and coupling with azo formers. Acridones do not open the ring during such reduction.

The above papers give apparently persuasive arguments in favor of the anthranilic structure of the above substances. Only the position of the chlorine atom in the reaction products remains unknown.

The product of the composition  $C_{14}H_{10}O_3NCl$  obtained from o-nitrobenzaldehyde and gualacol also formed an amino compound on reduction with zinc in acidic medium, the amino group in which was proven by diazotization of the product reduction, and the preparation of azo dyes with 8-naphthol and N-acid. Upon this basis, it is considered that the given compound also contains the anthranil group. The latter, however, is more correctly represented in the form of the benzisoxazole with an o-quinoid grouping of the benzene nucleus, which is confirmed by the bright yellow color of the substance obtained. For this reason, structure (III) was assigned to this compound:



The formation of this compound, evidently, is due to the rearrangement of the diphenylcarbinol derivative (IV) initially formed as a result of the condensation of 1 molecule of o-nitrobenzaldehyde with 1 molecule of gualacol. Such a rearrangement resembles that of o-nitrotoluene to anthranilic acid in its mechanism. The oxidative chlorination also occurred during this rearrangement, with the introduction of a chlorine into the o-nitroaldehyde nucleus.

## EXPERIMENTAL

### I. 3''-Nitro-3,3'-dimethoxy-4-hydroxyfuchsone

**Preparation of the leuco base.** A mixture of 21.0 g of m-nitrobenzaldehyde and 38.0 g of gualacol (10% excess of theory) was placed into a thick-walled vessel, saturated with dry hydrogen chloride (3.5 g), and left to stand for 10 days in the cold. At the end of the reaction, the mixture solidified into a continuous crystalline monolith, which was extracted and boiled several times with a 2% sodium carbonate solution until the product did not melt upon boiling. The yield was 46.5 g (88% of the theoretical). The crude product obtained was covered with 60% alcohol overnight, the product was filtered after 12 hours, washed with 60% alcohol, and dried in a

desiccator. The yield was 26.6 g (50.5% of the theoretical). The product was purified by recrystallization from 50% alcohol. The crude leuco base was also suitable for further processing. 3'-Nitro-3,3'-dimethoxy-4,4'-dihydroxytriphenylmethane was a prismatic light yellow crystalline substance which crystallized from concentrated and aqueous alcohol, acetic acid, benzene, and amyl acetate. After three recrystallizations from alcohol, m.p. 141.5°.

0.2616 g substance: 8.3 ml  $N_2$  (20°, 768.5 mm). 0.2518 g substance: 8.05 ml  $N_2$  (19.5°, 766.6 mm). Found %: N 3.65, 3.60.  $C_{21}H_{19}O_6N$ . Calculated %: N 3.69.

**Preparation of the hydroxyfuchson dye.** 5.0 g of the crude condensation production, treated once with a 2% sodium carbonate solution, was dissolved in 50 ml of amyl acetate. The solution was saturated with hydrogen chloride gas, and nitrogen dioxide, obtained by the cleavage of sodium nitrite with sulfuric acid, was passed in for 2 hours with a continuous stream of hydrogen chloride, and left to stand overnight. The crystals of the dye hydrochloride which formed, were filtered after 12 hours, washed with amyl acetate and ether, and air dried. The yield was 3.3 g (68.5% of the theoretical). When the crystalline leuco base was used for the oxidation, 5.51 g of the hydrochloride (98% of the theoretical) was obtained from 5.0 g. The hydrochloride of the fuchson was a violet crystalline substance with a greenish cast without a sharp melting point.

5.5 g of the hydrochloride was ground in a mortar with 80 ml of a 25% potassium acetate solution and 100 ml of water. The mixture was poured into a beaker and left to stand overnight. The next morning the red colored, friable precipitate of the hydrate form of the fuchson which formed was filtered, washed with water, and dried in a desiccator: yield, 4.6 g.

4.6 g of the hydrate form was recrystallized from 60 ml of glacial acetic acid with the acetic acid solution of the dye being boiled for a long time on a sand bath. 3.0 g of the fuchson crystallized (50.5% of the theoretical).

3'-Nitro-3,3'-dimethoxy-4-hydroxyfuchson was a red-orange prismatic crystalline substance which crystallized from glacial acetic acid and dry benzene. It melted at 229–229.5° after 3 recrystallizations from glacial acetic acid. The fuchson was dissolved in aqueous solutions of acids and alkalies to give a red-violet color in acids and a blue one in alkalies.

0.2880 g substance: 8.9 ml  $N_2$  (19.5°, 769.0 mm). 0.2520 g substance: 8.1 ml  $N_2$  (20°, 757.0 mm). Found %: N 3.53, 3.65.  $C_{21}H_{17}O_6N$ . Calculated %: N 3.68.

## II. 4''-Nitro-3,3'-dimethoxy-4-hydroxyfuchson

**Preparation of the leuco base.** A mixture of 4.9 g of p-nitrobenzaldehyde, 9.8 g of gualacol (20% excess), placed into a thick-walled vessel, was saturated with dry hydrogen chloride (0.7 g), and allowed to stand for 15 days in the cold; then the product was extracted and treated with boiling water. A light yellow product was obtained which was solid at ordinary temperatures but melted at 50–60°. It was used for the oxidation to the fuchson.

**Preparation of the hydroxyfuchson of the dye.** 5.0 g of the product treated as reported above, was dissolved in 60 ml of amyl acetate. The solution was saturated with hydrogen chloride and oxidized with nitrogen dioxide. Yield, 3.6 g of the hydrochloride (66% of the theoretical). The fuchson hydrochloride was a dark violet crystalline substance with a gold cast, without a sharp melting point.

3.6 g of the hydrochloride was ground in a mortar with 50 ml of 25% potassium acetate solution and 80 ml of water. The solution was transferred to a beaker and left to stand overnight. The brown red precipitate of the hydrate form of the fuchson which formed, was filtered after 12 hours, washed with water, and dried in a desiccator: yield, 3.0 g.

3.0 g of the hydrate form of the fuchson was recrystallized from 25 ml of glacial acetic acid with the acetic acid solution of the dye being boiled for a long time on a sand bath. 1.57 g of the free fuchson (48% of the theoretical) crystallized.

4''-Nitro-3,3'-dimethoxy-4-hydroxyfuchson was a dark red, prismatic crystalline substance which readily crystallized from glacial acetic acid and dry benzene. The product melted at 235–235.5° after 2 recrystallizations from glacial acetic acid. The fuchson dissolved in aqueous solutions of acid and alkalies to give a violet color in the acidic medium and a blue-green in alkaline.

0.2348 g substance: 7.75 ml  $N_2$  (20°, 756.4 mm). 0.2206 g substance: 7.0 ml  $N_2$  (19.5°, 758.6 mm). Found %: N 3.75, 3.62.  $C_{21}H_{17}O_6N$ . Calculated %: N 3.68.



### III. Condensation of o-Nitrobenzaldehyde with Gualacol

5.0 g of o-nitrobenzaldehyde mixed with 9.0 g of gualacol (10% excess) was placed in a thick-walled vessel and saturated with hydrogen chloride (1.1 g). After a 3 week standing, the viscous orange colored product was extracted from the vessel and covered with 15 ml of 70% alcohol overnight: the yellow precipitate was filtered after 12 hours, washed with 70% alcohol, and dried in a desiccator. Yield, 2.92 g.

The product was a gold-yellow, prismatic crystalline substance which crystallized from glacial acetic acid, benzene, ethyl acetate, amyl acetate, and alcohol. The product melted at 181.5° after 3 recrystallizations from glacial acetic acid.

0.2 g of the product was heated with 10 ml of concentrated hydrochloric acid and a pinch of zinc dust, and filtered. The filtrate was cooled and diazotized with crystalline sodium nitrite. The excess nitrous acid was decomposed with urea, using a starch iodide paper for control. The solution of the diazonium salt was coupled with  $\beta$ -naphthol dissolved in 10% sodium hydroxide, and with H-acid dissolved in 10% sodium carbonate. The product of the coupling with  $\beta$ -naphthol had a red color, that with H-acid, a red-violet.

0.1501, 0.1505 g substance: 0.0793, 0.0794 g AgCl. 0.1298, 0.1248 g substance: 0.1114, 0.1067 g AgCl. 0.1435 g substance: 6.3 ml  $N_2$  (20°, 756.4 mm), 0.1336 g substance: 6.05 ml  $N_2$  (19°, 768.0 mm). Found %: Cl 13.04, 13.10;  $OCH_3$  11.34, 11.30; N 4.98, 5.23.  $C_{12}H_9O_2NCl(OCH_3)$ . Calculated %: Cl 12.88;  $OCH_3$  11.25; N 5.08.

#### SUMMARY

The following nitro derivatives of dimethoxybenzaurin: 3'-nitro-3,3'-dimethoxy-4-hydroxyfuchson and 4'-nitro-3,3'-dimethoxy-4-hydroxyfuchson, were obtained by the condensation of m-nitrobenzaldehyde and p-nitrobenzaldehyde with gualacol in the presence of hydrogen chloride, followed by the oxidation of the leuco compound formed.

A substance of the composition  $C_{14}H_{11}O_2NCl$  was formed by the condensation of o-nitrobenzaldehyde with gualacol in the presence of hydrogen chloride, and must be considered to be an anthranil derivative similar to the products obtained by the condensation of o-nitrobenzaldehyde with phenol or dimethylaniline, reported in the literature. The formation of this substance results from the rearrangement of the diphenylcarbinol derivative formed initially during the condensation, followed by the cyclization of the isoxazole ring; such a rearrangement is similar in mechanism to that of o-nitrotoluene to anthranilic acid, and proceeds in the presence of hydrogen chloride accompanied by the simultaneous chlorination of the substance.

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Received March 19, 1953.

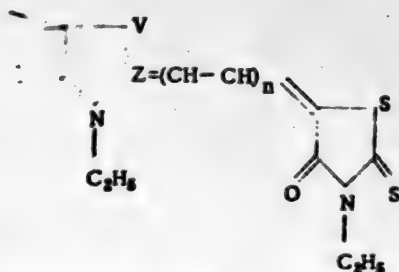
\* See Consultants Bureau Translation, page a-383.

# MEROCYANINE DYES, RHODANINE DERIVATIVES

## V. SEVERAL TETRA- AND HEXAMETHINEMEROCYANINE DERIVATIVES OF 3-ETHYLRHODANINE

M. V. Deichmeister, I. I. Levkoev, and E. B. Lifshits

In one of the previous investigations [1], it was shown that the absorption maximum of dimethinemerocyanine derivatives of 3-ethylrhodanine (I;  $n = 1$ ), as a rule, is shifted toward the longer wave lengths according to the increase in the basicity of the nitrogen heterocycle residue which is part of the dye molecule. Correspondingly, the value of the "hypsochromic shift" of the absorption maximum calculated for these dyes decreases.



$V = O, S, Se, -C(CH_3)_3, -CH=CH-, =N-CH_3$ , etc;  $Z = \text{hydrocarbon}$ , or the group  $CH=C=C$  (in the last case the group  $V$  is absent);  $n = 0, 1, 2$ , or  $3$ .

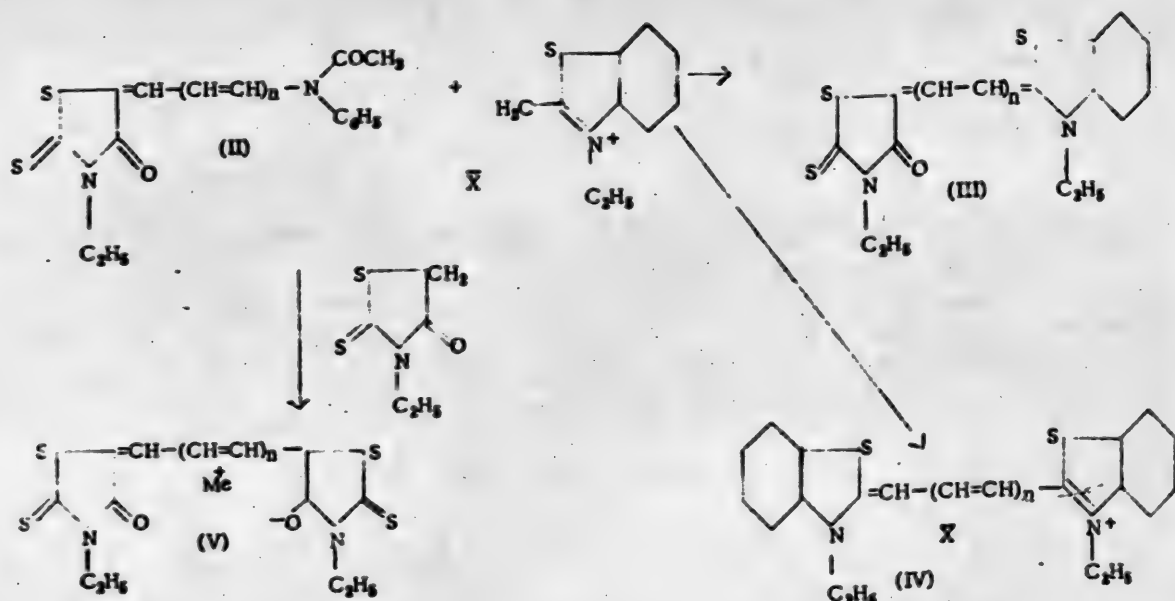
For this reason, it was suggested that the structure of similar dyes with small and moderately basic residues are more probably expressed by means of formula (I).

The relation of the color of the higher polymethinemerocyanine derivatives of rhodanine to their structure has scarcely been studied up to now. Several dyes of this series have been synthesized by Hammer [2] and Brooker [4, 5]. The latter author states that the hypsochromic shift of the absorption maximum increases upon going from the dimethine- to the tetramethinemerocyanine in the case of dyes with residues of low basicity [3, 5]. For this reason, it appeared of interest to investigate in greater detail the effect of the increase of the polymethine chain on the optical properties of these dyes and to study methods for their synthesis.

The present investigation is concerned with the synthesis of tetra- and hexamethinemerocyanine derivatives of 3-ethylrhodanine with residues of various degrees of basicity and the study of their optical properties. According to the literature, tetramethinemerocyanines are formed by the reaction of 3-ethylrhodanine with quaternary salts of 2- $\delta$ -acetanilino-butadienyl derivatives of heterocyclic nitrogen bases [2-7]. The possibility of obtaining polymethinemerocyanines by the condensation of 5- $\gamma$ -acetanilinoallylidene (II;  $n = 1$ ) and 5- $\epsilon$ -acetanilino-pentadienylidenerhodanines (II;  $n = 2$ ) with quaternary salts of 2(4)-methyl substituted heterocyclic nitrogen bases [6] was also mentioned. The latter method was found to be very convenient for the preparation of tetra- and hexamethinemerocyanine derivatives of 3-ethylrhodanine, because of which this method was studied in greater detail. It was found that similar dyes with 3,3-dimethylindolenyl, benzthiazo-yl, and quinolenyl(2) residues were readily obtained by the condensation of 5-acetanilinoallylidene- or 5-acetanilino-pentadienylidene-3-ethylrhodanine with quaternary salts of 2-methyl derivatives of the corresponding heterocyclic nitrogen bases in absolute alcoholic medium in the presence of an excess of triethylamine.

Almost in all cases during the investigation, small amounts of side dyes were isolated which were difficult to desorb from aluminum oxide and were poorly soluble in benzene. It was found that these dyes were the corresponding di- and tri-carbocyanines, as for example (IV) (compare [2]).

They were formed, evidently, as a result of the rupture of the bond between the carbon atoms in the acetanilino polymethine derivatives (compare [8]).



Tri- (compare [2]) and pentamethineoxanine derivatives of 3-ethylrhodanine (V;  $n = 1$  or  $2$ ) were also synthesized by the reaction of acetanilinoallylidene- and pentadienylidenetherhodanines (II) with 3-ethylrhodanine in pyridine in the presence of triethylamine, or in absolute ethyl alcohol in the presence of anhydrous potassium carbonate.

Salts of pentamethineoxanines (V,  $n = 2$ ) were very unstable and were rapidly decomposed upon boiling with alcohol. The free dye was more stable, and it could be obtained in pure state.

The absorption curves were measured for all of the dyes synthesized, and the values of the hypsochromic shift were calculated (in comparison to the arithmetic mean values of the absorption maxima of the corresponding dicarbocyanines and trimethineoxanines, or tricarbocyanines and pentamethineoxanines). These results are given in Table 1.

The absorption maxima of salts of mono-, tri-, and pentamethinecyanine derivatives of 3-ethylrhodanine (V) are 542, 613 m $\mu$  (613), and 714 m $\mu$  respectively. (The data of Brooker [5] for these dyes in methanol is given in parentheses).

As is apparent for Table 1, the intensity of the color of the dye increases upon going from the dimethinecyanine to the tetramethine derivative, which is greater the greater the basicity of the heterocyclic nitrogen residue. Further increase of the polymethine chain causes a much smaller bathochromic shift. Upon the introduction of the vinylene group into the polymethine chain of dimethinecyanine with 3,3-dimethylindolyl and 3,3-dimethylindolyl residues, the hypsochromic shift of the absorption maximum increases, whereas for dyes with quinoline residues, it decreases (from 6 to 1.5 m $\mu$ ) (compare [3,5]). The hypsochromic shift increases in all cases upon going to the hexamethine derivatives; the value of this shift is greater the less basic the heterocyclic nitrogen residue.

Upon examining the results obtained, the decrease of the value of the hypsochromic shift upon the introduction of a vinylene group into the polymethine chain of dimethinecyanines with residues of quinoline-(2) becomes apparent. This fact can be explained by different distribution of the electron density along the polymethine chain in the molecule of the dimethinecyanine with a quinoline-(2) residue in comparison to dyes containing 3,3-dimethylindolyl and benzthiazolyl residues. In order to answer the above question, it seemed of interest to

Table 1

Hetero- cyclic nitrogen residue	Dimethine- merocyanines		Tetramethine- merocyanines			Hexamethine- merocyanines			Carbo- cyan- ines	Di- carbo- cyan- ines	Tri- carbo- cyan- ines
	$\lambda_{\text{max.}}$ (in m $\mu$ )	Hypso- chromic shift (in m $\mu$ )	$\lambda_{\text{max.}}$ (in m $\mu$ )	Hypso- chromic shift (in m $\mu$ )	Vinyl- ene shift (in m $\mu$ )	$\lambda_{\text{max.}}$ (in m $\mu$ )	Hypso- chromic shift (in m $\mu$ )	Vinyl- ene shift (in m $\mu$ )			
										$\lambda_{\text{max.}}$ (in m $\mu$ )	
3,3-Dimethyl- indolenine	503(503)	41	574(566)	49.5	71	606	124	32	546	634 (641)	745
Benzthiazole	524(526)	26	607(605)	26.5	83	636	102.5	29	558	654 (650)	763
Quinoline-2	568(565)	6	660(663)	1.5	92	687	79.5	27	606	710 (707.5)	819

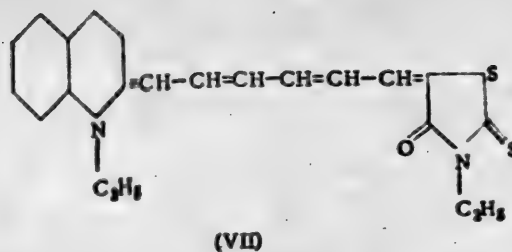
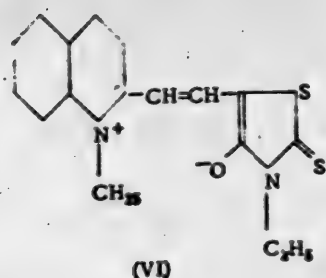
Table 2

Hetero- cyclic nitrogen residue	Absorption maxima of N-ethylates of dimethinemerocyanines with various heterocyclic residues (in m $\mu$ )							
	Methanol $\epsilon = 31.2$	Ethanol $\epsilon = 25.8$	Propanol $\epsilon = 22.2$	Butanol $\epsilon = 17.7$	Chloro- form $\epsilon = 4.64$	Benzene $\epsilon = 2.296$	Carbon- tetra- chloride $\epsilon = 2.19$	Hexane $\epsilon = 1.91$
3,3-Dimethyl- indolenine	502	503	502	502	502	490	486	470
Benzthiazole	522	524	522	522	522	512	502	488
Benzoxazole	493	492	492	493	490	480	474	460
Thiazoline	481	482	481	483	480	472	464	450
Thiazole	531	532	532	533	530	522	514	496
Pyridine-2	538	542	544	545	543	530	514	500
Quinoline-2	562	568	566	568	570	560	-	-
1-Methylbenz- imidazole	508	511	512	513	517	511	-	-

investigate the change of the position of the absorption maxima of dimethine merocyanine derivatives of 3-ethylrhodanine (I,  $n = 1$ ) in various solvents, the polarity of which, as it is known, noticeably effects the electronic structure, and therefore, the color of the intramolecular dyes [9-13]. The data obtained are given in Table 2.

As it is apparent from Table 2, upon going from methanol to less polar solvents, the absorption maxima of dimethinemerocyanines with residues of small and moderate basicity is gradually shifted toward the lower wavelengths. In cases of dyes with pyridine, quinole, and 1-methylbenzimidazole residues, a bathochromic shift of the absorption maximum first occurs, and then, the increase of the color. These results confirmed the previous suggestion [1] that the electron density is gradually equalized along the polymethine chain in the molecule with the increase of the basicity of heterocyclic residue for the dyes investigated, as well as for the derivatives of 3-hydroxythionaphthene [12]. The structures of the dimethinemerocyanines with pyridine, quinoline, and 1-methylbenzimidazole residues in ethyl alcohol, evidently, are more correctly expressed by an intramolecular formula, for example (VD).

\* In carbon tetrachloride and hexane, the color rapidly disappeared.



From this point of view, the generalities established for tetra- and hexamethinemerocyanines become more comprehensible.

Upon the increase of the internal chain of the merocyanines, their polarity decreases, and in all cases, the electronic shift from the nitrogen atom along the polymethine chromophore gradually decreases. In the dyes investigated containing indolenine and benzthiazole residues (in ethyl alcohol), the distribution of the electron density along the chain becomes less and less equalized, which is confirmed by the subsequent increase of the values of the hypsochromic shift of the absorption maxima. In the case of the highly polar quinomerocyanine, upon going from the di- to the tetramethine derivatives in ethyl alcohol, on the other hand, a more equivalent distribution of the electron density along the chain is attained, which upon further increase in the length of the chromophore is again broken because of which the structure of hexamethinemerocyanines in ethyl alcohol can be expressed by formula (VII). For this reason, the value of the hypsochromic shift of the absorption maximum in this group of dyes at first decreases and then increases once more.

#### EXPERIMENTAL

**3-Ethyl-5- $\gamma$ -acetanilinoallylidenerhodanine [2,6].** It was prepared by heating 0.32 g of 3-ethylrhodanine with 0.52 g of malonaldehyde dianil hydrochloride in 3 ml of acetic anhydride for 1 hour. The precipitate which formed was filtered after 12 hours, and washed with water and alcohol. Weight, 0.54 g; m.p., 215–217°. The yield was 0.45 g (67.7%) after recrystallization from ethyl alcohol (1 g from 600 ml). Dark red shiny prisms m.p. 224–225° (with decomposition) (225.5–226.5° [6]).

Found %: N 8.36.  $C_{18}H_{15}O_2N_2S_2$ . Calculated %: N 8.42.

**3-Ethyl-5- $\epsilon$ -anilinopentadienylidenerhodanine [6].** A mixture of 0.16 g of 3-ethylrhodanine, 0.28 g of glutaraldehyde dianil hydrochloride, 2 ml absolute ethyl alcohol, and 0.1 g triethylamine were heated for 5 minutes on the boiling water bath. The precipitate which formed was filtered after 6 hours and washed with alcohol. Weight, 0.23 g; m.p. 192–193°. The yield was 0.2 g (63.2%) after recrystallization from ethyl alcohol (1 g from 120 ml). Blue-violet platelets with m.p. 193° (with decomposition).

Found %: N 8.97.  $C_{18}H_{15}ON_2S_2$ . Calculated %: N 8.85.

**3-Ethyl-5- $\epsilon$ -acetanilinopentadienylidenerhodanine [6].** A solution of 0.23 g of 3-ethyl-5- $\epsilon$ -anilinopentadienylidenerhodanine in 7 ml of acetic anhydride was refluxed for 5 minutes in a flask. The precipitate which formed upon cooling was filtered after 12 hours and washed with water and alcohol. Weight, 0.18 g; m.p. 186–188°. The yield was 0.16 g (44.7%) after recrystallization from ethyl alcohol (1 g from 75 ml). Brownish shining platelets with m.p. 190–191° (with decomposition).

Found %: N 7.81.  $C_{18}H_{15}O_2N_2S_2$ . Calculated %: N 7.81.

**3-Ethyl-5-[ $\delta$ -(3'-ethylbenzthiazolynylidene-2')-butenylidene]-thiazolidinethione-(2)-one-(4) [2,4,7].** A mixture of 0.32 g of 3-ethyl-5- $\gamma$ -acetanilinoallylidenerhodanine, 0.44 g of 2-methylbenzthiazole ethiodide, 20 ml of absolute ethyl alcohol, and 0.31 g of triethylamine was boiled for 30 minutes. The precipitate which formed was filtered and washed with alcohol. Weight, 0.32 g; m.p. 211–214° (with decomposition).

\* The yield here and subsequently is expressed in percent of the theoretical.



position). The product was boiled with 40 ml of ethyl alcohol, the insoluble residue was filtered, and recrystallized from 30 ml of benzene. Yield, 0.14 g (37.4%); m.p. 238–239° (with decomposition). For final purification, a benzene solution of the dye was filtered through a layer of aluminum oxide, upon which a small amount of a blue side product was strongly adsorbed. The benzene solution was evaporated in vacuum until the beginning of crystallization, the dye was filtered and washed with alcohol. Weight, 0.1 g. Dark blue needles with m.p. 238–239° (with decomposition) (239–241° [4], 238° [2]).

Found %: N 7.29,  $C_{15}H_{12}ON_2S_2$ . Calculated %: N 7.48.

0.11 g of a substance was isolated from the wash alcohol, which was obtained in the form of green shiny needles with m.p. 249–250° after three boilings with benzene and recrystallizations from methyl alcohol.

The absorption curve in ethyl alcohol, as well as the position of the absorption maximum (at 654 mμ) of the given product and those of 3,3'-diethylthiadicarbocyanine iodide coincided completely.

3-Ethyl-5-[ $\zeta$ -(3'-ethylbenzthiazolinyldiene-2')-hexadienyldiene]-thiazolidinethione-(2)-one-(4) [4, 6]. It was prepared by heating a mixture of 0.35 g of 3-ethyl-5- $\epsilon$ -acetanilino-pentadienyldenerhodanine, 0.6 g of 2-methylbenzthiazole ethiodide, 10 ml of absolute ethyl alcohol, and 0.42 g of triethylamine for 20 minutes. Weight, 0.2 g; m.p. 209–210° (with decomposition). The yield was 0.14 g (35%) after washing with boiling ethyl alcohol (2 times with 25 ml), crystallization from benzene (1 g from 500 ml); m.p. 223–224° (with decomposition). The weight of the purified merocyanine was 0.1 g after removal of the blue-green side product upon aluminum oxide.

Green needles with m.p. 223–224° (with decomposition) (231–233° [4]).

Found %: N 7.04,  $C_{20}H_{16}ON_2S_2$ . Calculated %: N 6.99.

0.08 g of a substance separated upon standing from the wash alcohol, which, upon boiling with benzene and recrystallization from ethyl alcohol, was obtained in the form of green needles with a golden sheen with m.p. 210–212° (m.p. of 3,3'-diethylthiadicarbocyanine iodide is 210–212° [11]). The sensitization maximum was 810 mμ.

3-Ethyl-5-[ $\delta$ -(1'-ethyl-3',3'-dimethylindolinyldiene-2')-butenyldiene]-thiazolidinethione-(2)-one-(4). [5]. A mixture of 0.32 g of 3-ethyl-5- $\gamma$ -acetanilinoallyldenerhodanine, 0.31 g of 2,3,3-trimethylindoline ethiodide, 2 ml of butanol, 1 ml of pyridine, and 0.1 g of triethylamine was heated for 2.5 hours at 120°. On the following day, the precipitate which formed was filtered and washed with alcohol. Weight 0.19 g; m.p. 155–157° (with decomposition). The yield was 0.13 g (38.8%) after recrystallization from ethyl alcohol (1 g from 90 ml). For final purification, a benzene solution of the dye was filtered through a layer of aluminum oxide upon which the blue-violet side product was adsorbed. 0.08 g of the substance in the form of grey, shiny prisms with m.p. 166–167° (with decomposition) (176–178° [5]) was obtained from the benzene solution after evaporation in vacuum.

Found %: N 7.06,  $C_{21}H_{20}ON_2S_2$ . Calculated %: N 7.28.

3-Ethyl-5-[ $\zeta$ -(1'-ethyl-3',3'-dimethylindolinyldiene-2')-hexadienyldiene]-thiazolidinethione-(2)-one-(4). A mixture of 0.7 g of 3-ethyl-5- $\epsilon$ -acetanilino-pentadienyldenerhodanine, 2.1 g of ethyl-p-tolylsulfonate of 2,3,3-trimethylindoline, 4 ml butanol, 2 ml pyridine, and 0.42 g of triethylamine were heated for 2 hours at 130°. 3 ml of ethyl alcohol was then added, and the liquid cooled with ice. The dye which precipitated was filtered after 12 hours and washed with alcohol. Weight, 0.17 g; m.p. 169–172° (with decomposition). After recrystallization from propanol (1 g from 100 ml) and filtration through a layer of aluminum oxide, with which the removal of impurities of a blue side product was accomplished, 0.14 g of a substance (17%) was obtained in the form of green, shiny prisms with m.p. 182° (with decomposition).

Found %: N 6.96,  $C_{22}H_{20}ON_2S_2$ . Calculated %: N 6.82.

3-Ethyl-5-[ $\delta$ -(1'-ethyl-dihydroquinolidene-2')-butenyldiene]-thiazolidinethione-(2)-one-(4) [2, 5]. A mixture of 0.32 g 3-ethyl-5- $\gamma$ -acetanilinoallyldenerhodanine, 0.6 g of quinaldine ethiodide, 8 ml of absolute ethyl alcohol, and 0.42 g of triethylamine were boiled for 30 minutes. The precipitate which formed was filtered after 6 hours and washed with alcohol. Weight 0.32 g; m.p. 202–212° (with decomposition). After boiling with 50 ml of ethyl alcohol, the insoluble residue was recrystallized from benzene (1 g from 500 ml). Yield 0.08 g (21.7%); m.p. 253–255° (with decomposition). For a final purification, a benzene solution of the dye was filtered through a layer of aluminum oxide, upon which an impurity of green side product was adsorbed. 0.4 g of a substance was obtained in the form of blue prisms with m.p. 253–255° (with decomposition) (253–255° [5], 270° [2]).

Found %: N 7.50,  $C_{28}H_{22}ON_2S_2$ . Calculated %: N 7.60.

3-Ethyl-5-[5-(1'-ethyl-4'-hydroxythiazolinylidene-2')-hexadienylidene]-thiazolidine-thione-(2)-one-(4). A mixture of 0.35 g of 3-ethyl-5- $\epsilon$ -acetanilino-pentadienylidenerhodanine, 0.6 g of quinaldine ethiodide, 10 ml of absolute ethyl alcohol, and 0.42 g of triethylamine were boiled for 30 minutes. The dye which precipitated was filtered after 6 hours and washed with alcohol. Weight 0.35 g; m.p. 191° (with decomposition). The yield was 0.16 g (40.5%) after washing the dye with 10 ml of boiling alcohol and recrystallization of the residue from 155 ml of ethyl alcohol and then from a mixture of ethyl alcohol and benzene (1:1) (1 g from 625 ml); m.p. 226–227° (with decomposition). The final purification of the dye was accomplished by filtration through aluminum oxide, whereby small impurities of a green side product were removed. Green shiny prisms with m.p. 226–227° (with decomposition).

Found %: N 6.90,  $C_{22}H_{22}ON_2S_2$ . Calculated %: N 7.10.

3-Ethyl-5-[3'-ethyl-4'-hydroxythiazolinthion-(2)-yl-5'-allylidene]-thiazolidine-thione-(2)-one-(4) [2, 7]. A mixture of 0.66 g of 3-ethyl-5- $\gamma$ -acetanilinoallylidenerhodanine, 0.64 g of 3-ethylrhodanine, 8 ml of pyridine, and 0.82 g of triethylamine was heated for 2 hours at 130°. The cooled reaction solution was treated with 150 ml of ether. The precipitate which formed was filtered after 12 hours and washed with ether. Weight, 0.3 g; m.p. 156–157°. For purification, the triethylammonium salt was recrystallized from aqueous alcohol (3:1) (1 g from 60 ml). Yield 0.2 g (21.9%). Golden platelets with m.p. 170–171° (with decomposition).

Found %: N 9.23,  $C_{15}H_{12}O_2N_2S_4$ . Calculated %: N 9.12.

15 ml of concentrated hydrochloric acid (d 1.18) was added to a solution of 0.46 g of the triethylammonium salt in 100 ml of 50% aqueous alcohol. The precipitate which formed was filtered, washed with water and alcohol, and then crystallized from glacial acetic acid (1 g from 85 ml) after drying. Yield, 0.15 g (41.8%). Yellow needles with m.p. 128–130° (with decomposition). (According to Hamer and Winton, it liquifies at 160° and decomposes at 210° [2]).

Found %: N 7.69,  $C_{15}H_{14}O_2N_2S_4$ . Calculated %: N 7.81.

3-Ethyl-5-[3'-ethyl-4'-hydroxythiazolinthion-(2)-yl-5'-pentadienylidene]-thiazolidine-thione-(2)-one-(4). A mixture of 0.33 g of 3-ethyl-5- $\epsilon$ -acetanilino-pentadienylidenerhodanine, 0.32 g of 3-ethylrhodanine, 5 ml of absolute ethyl alcohol, and 0.27 g of anhydrous potassium carbonate was boiled for 15 minutes. The unreacted potassium carbonate was filtered, and 50 ml of absolute ether was added to the filtrate. The precipitated potassium salt was filtered on the following day and washed with ether. Weight 0.36 g; m.p. 146–150° (with decomposition). It was readily soluble in alcohol, noticeably in water, and difficultly in ether. Upon boiling with alcohol, the salt of the dye was decomposed. 2 ml of glacial acetic acid was added to a suspension of 0.42 g of the above salt in 100 ml of water. The flocculent precipitate was filtered and washed with water and alcohol. Weight, 0.32 g; m.p. 135–147°. The yield was 0.14 g (38.4%) after three recrystallizations from glacial acetic acid (1 g from 20 ml). Red brown needles with m.p. 168–170° (with decomposition). It was very readily soluble in benzene and ether, and almost insoluble in ethyl alcohol.

Found %: N 7.48,  $C_{15}H_{16}O_2N_2S_4$ . Calculated %: N 7.28.

The authors wish to express their deepest gratitude to S. V. Natanson for a series of valuable suggestions and advice.

#### SUMMARY

1. The syntheses of several tetra- and hexamethinemerocyanine derivatives of 3-ethylrhodanine, as well as the corresponding tri- and pentamethineoxanines was effected.
2. The absorption spectra of eight dimethinemerocyanine derivatives of 3-ethylrhodanine, differing in the nature of the nitrogen heterocycle residue, were measured in various solvents.
3. On the basis of the investigation of the absorption spectra of the merocyanine derivatives of 3-ethylrhodanine, it was shown that the distribution of the electron density in their chromophores can vary considerably, in relation to the basicity of the heterocyclic residues and the length of the internal polymethine chain.

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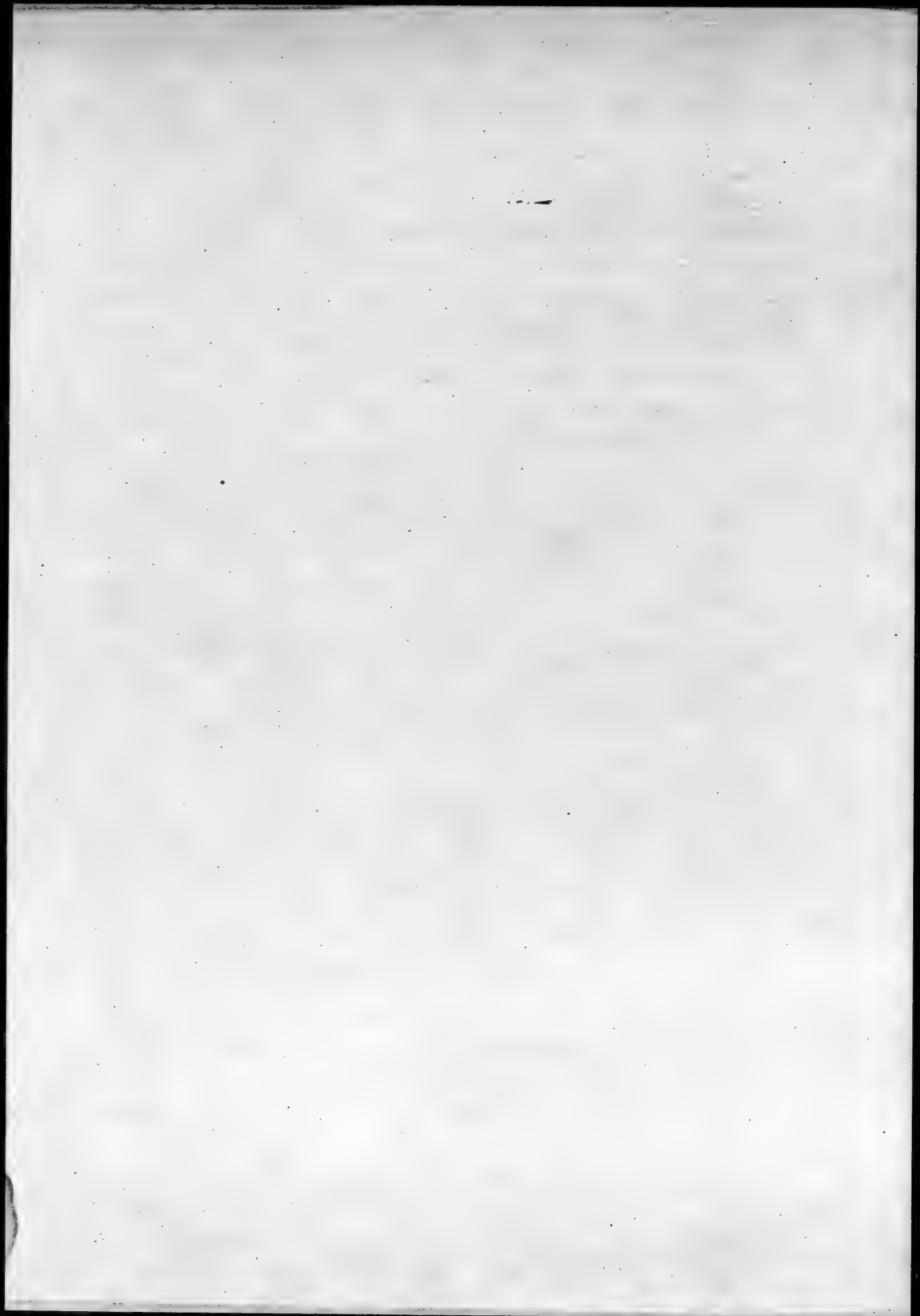
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Received April 4, 1953

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# STUDY OF THE SULFONATION REACTION

## XXXIII. EQUILIBRIUM BETWEEN SULFONIC ACIDS AND THEIR ACID CHLORIDES

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The equilibrium between various mono- and polysulfonic acids on the one hand, and their acid chlorides, on the other, was previously studied by the authors [1,2] in a medium consisting of a mixture of sulfuric and chlorosulfonic acids, which was established according to the equation:



The results of the study of the equilibrium between sulfonic acids and their acid chlorides containing various functional groups, carboxylic, nitro, and a second sulfonic, in the benzene nucleus are reported below.

Equilibrium between m-nitrobenzenesulfonic derivatives. m-Nitrobenzenesulfonyl chloride, recrystallized from glacial acetic acid, with m.p. 61.5–62°, was dissolved in a mixture of sulfuric and chlorosulfonic acids of various composition. The solutions were kept over phosphorus pentoxide for 10 hours at 70 ± 0.5°. After pouring onto ice, the acid chloride was filtered, washed, dried, and weighed. The results of experiment 172, given in Table 1, show that even after 3 hours of standing, the system was close to the equilibrium composition. The chloride isolated from the equilibrium mixture had a m.p. of 61.5–62°.

TABLE 1

Composition of the Equilibrium between m-Nitrobenzenesulfonic Acid and Its Acid Chloride at 80°

Expt. No.	Moles used per mole of chloride		Time (in hours)	Chloride obtained (in % of that used)	Equilibrium constant K
	H <sub>2</sub> SO <sub>4</sub>	HSO <sub>3</sub> Cl			
174	1.36	3.54	10	85.5	0.52
168	1.48	2.14	10	78.7	0.50
169	1.92	2.07	10	74.9	0.47
			3	56.0	
172	3.06	1.52	6	58.7	0.51
			10	58.9	0.51
166	3.31	0.72	10	47.0	0.51
173	4.91	0.82	10	38.0	0.55
Average					0.51

If for 1 mole of the acid chloride,  $\underline{m}$  moles of sulfuric acid and  $\underline{n}$  moles of chlorosulfonic acid are taken, then after achieving equilibrium according to the equation:



$$1-x \quad m-x \quad x \quad n+x$$

the equilibrium constant can be calculated:

$$K = \frac{[x][n+x]}{[1-x][m-x]} \quad (\text{II})$$

The experimental results showed that the equilibrium constant kept practically a constant value at various ratios of sulfuric and chlorosulfonic acids.

The amount of sulfonic acid in the equilibrium mixture is calculated according to the formula:

$$x = \frac{n+K}{2(K-1)} = \frac{Km \pm \sqrt{(n+K+Km)^2 - (4K-1)Km}}{2(K-1)} \quad (\text{III})$$

Table 2 gives the amount of the acid chloride (1-x), calculated according to formula (III), and the values found experimentally.

Comparison of the results shows that the difference between the calculated and experimentally found amounts of acid chloride in the equilibrium mixture do not exceed 1.4%.



TABLE 2

Equilibrium between m-Nitrobenzenesulfonic Acid and Its Acid Chloride

Expt. No.	Sulfonyl chloride in the mixture (in % of that taken)	
	Found	Calculated
174	85.5	85.6
168	78.7	78.5
169	74.9	73.5
172	58.8	58.8
166	47.0	47.0
173	38.0	39.4

Equilibrium between m-sulfobenzoic acid and its chloride. The chloride of m-sulfobenzoic acid was recrystallized from dichloroethane until a m.p. of 133–134.5° was attained. Experiments on the study of the equilibrium were effected in the same manner as those reported for nitrobenzenesulfonic acid by keeping the mixture at 80° for 10 hours. The chloride isolated from the equilibrium mixture had a m.p. of 127–130°. The decrease in the melting point of the chloride resulted from the partial hydrolysis of the moist substance during its drying in the desiccator over sodium hydroxide. The melting point of the pure chloride was decreased in the same manner after moistening and drying.

The experimental results given in Table 3 made it possible to find the equilibrium constant according to formula (II), and to find the amount of chloride in the mixture, according to formula (III) by means of its value, equal to 1.22, for comparison with that isolated experimentally.

TABLE 3

Equilibrium between Sulfobenzole Acid and Its Acid Chloride at 80°

Expt. No.	Moles used per mole of chloride		Chloride isolated (in % of that used)	Equilibrium constant K	Chloride in the mixture calculated according to formula (III) (in % of that used)
	H <sub>2</sub> SO <sub>4</sub>	HSCl <sub>2</sub>			
204	1.62	4.05	69.8	1.43	72.4
207	1.59	3.37	69.7	1.24	70.1
205	2.01	2.99	62.4	1.27	62.7
201	2.93	2.70	51.6	1.22	51.6
202	3.77	1.73	38.6	1.19	37.9
203	3.96	1.26	36.6	0.99	32.5
Average				1.22	

Equilibrium between 2,4-toluenedisulfonic derivatives.

The chloride of 2,4-toluenedisulfonic acid was recrystallized from ether until a m.p. of 52° was attained. Experiments on the study of the equilibrium were conducted in the same manner as for nitrobenzenesulfonic acid by keeping the mixture at 80° for 10 hours. The chloride isolated from the equilibrium mixture had a m.p. of 52°. The experimental results are given in Table 4. As with the above, the amount of chloride in the mixture was calculated from the equilibrium

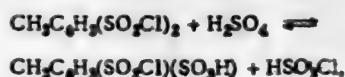
constant according to formula (III) and compared with that found experimentally (see Table 4).

TABLE 4

Equilibrium between 2,4-Toluenedisulfonic Acid and Its Acid Chloride at 80°

Expt. No.	Moles used per mole of chloride		Chloride isolated (in % of that used)	Equilibrium constant K	Chloride in the mixture calculated according to formula (II) (in % of that used)
	H <sub>2</sub> SO <sub>4</sub>	HSO <sub>3</sub> Cl			
192	1.05	4.23	86.6	0.74	84.5
188	1.92	3.10	71.8	0.80	70.1
198	2.45	3.20	63.7	1.00	65.2
189	2.92	2.25	57.9	0.77	55.0
190	3.33	1.83	44.7	1.06	48.0
191	3.70	2.00	44.0	1.04	47.1
Average				0.90	

As previously reported [2], the equilibrium in this case is established according to the equation:



i.e., the sulfonic acid sulfonyl chloride is formed, which can be further transformed into the disulfonic acid. For this reason,  $x$  corresponds to the number of moles of the disulfonyl chloride transformed into the sulfonic acid sulfonyl chloride.

A total of 7 cases of equilibrium between sulfonic acids and their acid chlorides have been studied by the authors [1, 2]. A comparison of results obtained is

given below. If, according to equation (I), 1 mole of sulfuric acid was used per mole of the chloride, then the amount of the chloride transformed into the sulfonic acid will be about 50%, with a variation of 8% in one or the other direction, as is shown in Table 5.

TABLE 5

Equilibrium between Sulfonic Acids and Their Acid Chlorides at Equimolar Ratios of the Chloride to Sulfuric Acid

Acid chlorides	K	Amount transformed into the sulfonic acid (in %)
m-Nitrobenzenesulfonyl chloride	0.51	41.7
p-Dichlorobenzenesulfonyl chloride	0.67	45.0
p-Toluenesulfonyl chloride	1.18	52.1
Chloride of m-sulfobenzoic acid	1.22	52.5
2,4-Toluenedisulfonyl chloride	0.90	48.7
m-Benzenedisulfonyl chloride	1.33	53.6
1,3,5-Naphthalenetrisulfonyl chloride	1.90	57.9

The values of the constants for di- and trisulfonic acids, as a rule, are greater than for the monosulfonic derivatives.

## SUMMARY

The equilibria between m-nitrobenzenesulfonic acid and its acid chloride, m-sulfobenzoic acid and its acid chloride, and 2,4-toluenedisulfonic acid and its acid chloride were studied in a medium consisting of sulfuric and chlorosulfonic acids at 80°. The equilibrium constants found were equal to 0.51, 1.22, and 0.90, respectively.

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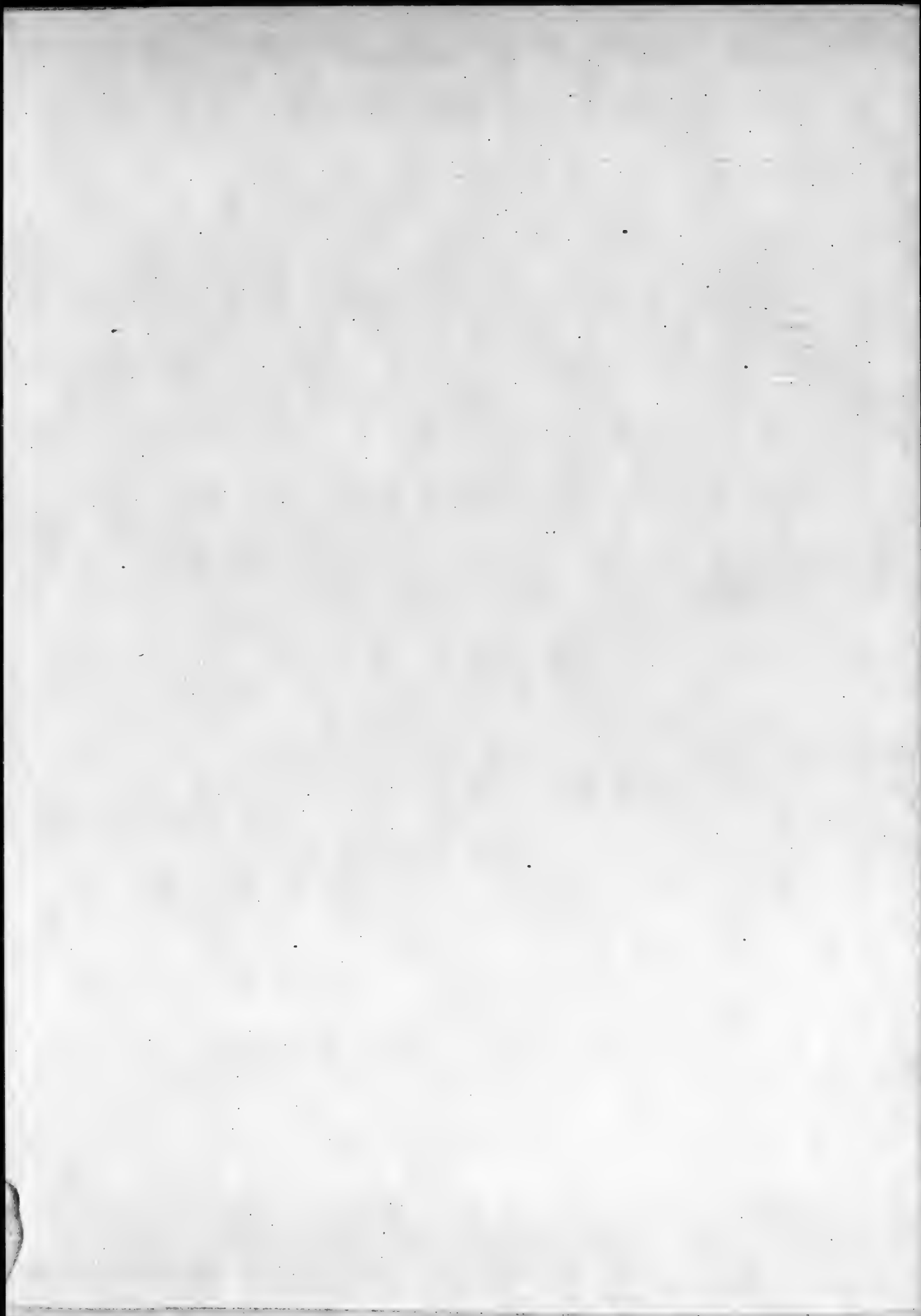
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Received March 28, 1953

The Ivanovsk Institute of Chemical Technology and the Ivanovsk State Institute of Medicine.

• See Consultants Bureau Translation, page. 787.



## ORGANIC INSECTOFUNGICIDES

### XVI. SYNTHESIS OF SUBSTITUTED ESTERS OF THIOPHOSPHORIC ACIDS CONTAINING VARIOUS FUNCTIONAL GROUPS IN THE AROMATIC RADICAL

M. L. Galashina and N. N. Melnikov

Recently it was shown that the introduction of a simple substituent such as a halide and alkoxy into the aliphatic radicals of one of the more active insecticides, diethyl-4-nitrophenylthiophosphate, leads to a decrease in insecticidal activity of the compound [1]. It appeared of undoubted interest to study the effect of the introduction of various substituents into the aromatic radical of dialkylarylthiophosphates on the insecticidal activity.

The synthesis of alkylarylthiophosphates containing alkoxy, halide, thiocyno, and alkoxy and halide groups at the same time in the aromatic radical is reported in the present communication. The synthesis of alkoxy-aryldialkylthiophosphates is of interest because of structural resemblance of the esters of alkylresorcin with the known preparation "Potazan", which has found application in agriculture [2]. The compounds obtained and their properties are given in the Table.

Almost all of the compounds given in the Table are not reported in the literature; diethyl-4-methoxyphenylthiophosphate is the exception, whose synthesis has been given in entomological literature [3].

The synthesis of the compounds given in the Table was effected by means of the following reactions:



Tests of the dialkylarylthiophosphates conducted upon grain weevils and harmful beetles, showed that the insecticidal activity of dialkylalkoxyphenylthiophosphates was destroyed with the increase of the molecular weight of the alkoxy radical (starting with propyl).

A decrease of the insecticidal activity also occurs with the increase of the molecular weight of the ester aliphatic radical. It is interesting that the introduction of the thiocyno group in place of the nitro group sharply decreases the insecticidal activity of the compounds, while the introduction of the thiocyno group into the molecule of simple ester increases the insecticidal activity of the compounds sharply. The introduction of a halide into the dialkylalkoxyphenylthiophosphates increases the insecticidal activity of the compounds somewhat. All of the compounds given in the Table were found to be less active than diethyl-4-nitrophenylthiophosphate.

#### EXPERIMENTAL

The preparation of the dialkylarylthiophosphates was conducted under conditions reported in one of the previous communications [4]. An equimolecular amount of the dialkylchlorothiophosphate was added gradually with efficient stirring to the dry phenol wetted with chlorobenzene to which 1-2 drops of pyridine were added initially. The reaction mixture was then kept for several hours at 110-130°. The sodium chloride was filtered after the end of the reaction and the cooling of the reaction mixture, the filtrate washed with sodium hydroxide and water, and

Experiment No.	Name and Formula	Boiling point		$d_4^{25}$	$n_D^{25}$	Amount of phosphorus (in %)		Yield (in % of the theoretical)
		C	mm			Found	Calculated	
1	Diethyl-2-methoxyphenylthiophosphate ( $C_2H_5O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> -(2) . . . . .	170-174	8	1.1672	1.5990	10.90, 11.43	11.23	24
2	Diethyl-3-methoxyphenylthiophosphate ( $C_2H_5O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> -(3)	97	0.02	1.1483	1.5050	11.35, 11.50	11.23	56
3	Diethyl-3-ethoxyphenylthiophosphate ( $C_2H_5O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub> -(3)	170-180	8	1.1282	1.5045	11.20, 11.06	10.7	21
4	Diethyl-3-propyloxyphenylthiophosphate ( $C_2H_5O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OC <sub>3</sub> H <sub>7</sub> -(3)	170-180	8	1.1020	1.5038	10.1, 9.8	10.2	26
5	Diethyl-3-butyloxyphenylthiophosphate ( $C_2H_5O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OC <sub>4</sub> H <sub>9</sub> -(3)	140-150	0.35	1.1001	1.5028	9.7, 9.4	9.75	17
6	Diethyl-3-benzyloxyphenylthiophosphate ( $C_2H_5O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> -(3)	140-145	0.05	1.1645	1.5620	8.3, 8.5	8.8	25
7	Dipropyl-2-methoxyphenylthiophosphate ( $C_3H_7O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> -(2)	117	0.05	1.1288	1.5120	9.92, 10.10	10.19	24
8	Dipropyl-3-methoxyphenylthiophosphate ( $C_3H_7O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> -(3)	130-150	3	1.1106	1.4942	10.56, 10.36	10.19	18
9	Dipropyl-3-ethoxyphenylthiophosphate ( $C_3H_7O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub> -(3)	110-118	0.05	1.0949	1.4920	9.65, 9.80	9.75	18
10	Dipropyl-3-propyloxyphenylthiophosphate ( $C_3H_7O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OC <sub>3</sub> H <sub>7</sub> -(3)	120-146	0.35	1.0790	1.4995	9.15, 8.90	9.28	25
11	Dipropyl-3-butyloxyphenylthiophosphate ( $C_3H_7O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OC <sub>4</sub> H <sub>9</sub> -(3)	136-141	0.05	1.0754	1.5040	8.76, 8.50	8.96	14
12	Diethyl-4-methoxyphenylthiophosphate ( $C_2H_5O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> -(4)	117-122	0.1	1.1910	1.5180	10.75, 11.00	11.23	46
13	Diethyl-4-ethoxyphenylthiophosphate ( $C_2H_5O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub> -(4)	135-140	0.1	1.1400	1.5140	10.70, 10.80	10.73	23
14	Diethyl-4-propyloxyphenylthiophosphate ( $C_2H_5O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OC <sub>3</sub> H <sub>7</sub> -(4)	136	0.3	1.1086	1.5080	10.65, 10.70	10.19	22
15	Diethyl-4-butyloxyphenylthiophosphate ( $C_2H_5O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OC <sub>4</sub> H <sub>9</sub> -(4)	153	0.2	1.0905	1.5082	9.30, 9.25	9.75	46
16	Diethyl-2-bromo-4-ethoxyphenylthiophosphate ( $C_2H_5O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>3</sub> Br-(2)-OC <sub>2</sub> H <sub>5</sub> -(4)	142-150	0.02	1.3596	1.5410	8.00, 8.00	8.40	20
17	Diethyl-2-chloro-4-ethoxyphenylthiophosphate ( $C_2H_5O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>3</sub> Cl-(2)-OC <sub>2</sub> H <sub>5</sub> -(4)	110-126	0.15	1.2391	1.5285	9.16, 9.42	9.56	11
18	Diethyl-4-thiocyanophenylthiophosphate ( $C_2H_5O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> CNS-(4)	130	0.04	1.2121	1.5510	10.63, 10.25	10.47	10
19	Dimethyl-3-ethoxyphenylthiophosphate ( $CH_3O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub> -(3)	100-107	0.02	1.1970	1.5280	11.53, 11.37	11.82	18
20	Dipropyl-4-methoxyphenylthiophosphate ( $C_3H_7O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> -(4)	124	0.07	1.1201	1.5100	10.30, 10.15	10.43	48
21	Dipropyl-4-ethoxyphenylthiophosphate ( $C_3H_7O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub> -(4)	112-120	0.025	1.0956	1.5070	9.50, 9.35	9.75	52
22	Dipropyl-4-propyloxyphenylthiophosphate ( $C_3H_7O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OC <sub>3</sub> H <sub>7</sub> -(4)	148-150	0.2	1.0221	1.4970	9.75, 9.90	9.33	10
23	Dipropyl-4-butyloxyphenylthiophosphate ( $C_3H_7O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>4</sub> OC <sub>4</sub> H <sub>9</sub> -(4)	112-120	0.025	1.0082	1.4950	8.75, 8.60	8.96	30
24	Dipropyl-2-bromo-4-ethoxyphenylthiophosphate ( $C_3H_7O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>3</sub> Br-(2)-OC <sub>2</sub> H <sub>5</sub> -(4)	136-140	0.05	1.3113	1.5290	8.2, 8.2	7.80	35
25	Dipropyl-2-chloro-4-ethoxyphenylthiophosphate ( $C_3H_7O$ ) <sub>2</sub> PSOC <sub>6</sub> H <sub>3</sub> Cl-(2)-OC <sub>2</sub> H <sub>5</sub> -(4)	121-126	0.05	1.1883	1.5285	9.30, 9.30	8.79	19



water, and dried over sodium, or magnesium sulfates. The chlorobenzene was removed in vacuum, and the residue fractionated in vacuum.

The determination for phosphorous was conducted photocolrimetrically; sulfur, according to Carius.

#### SUMMARY

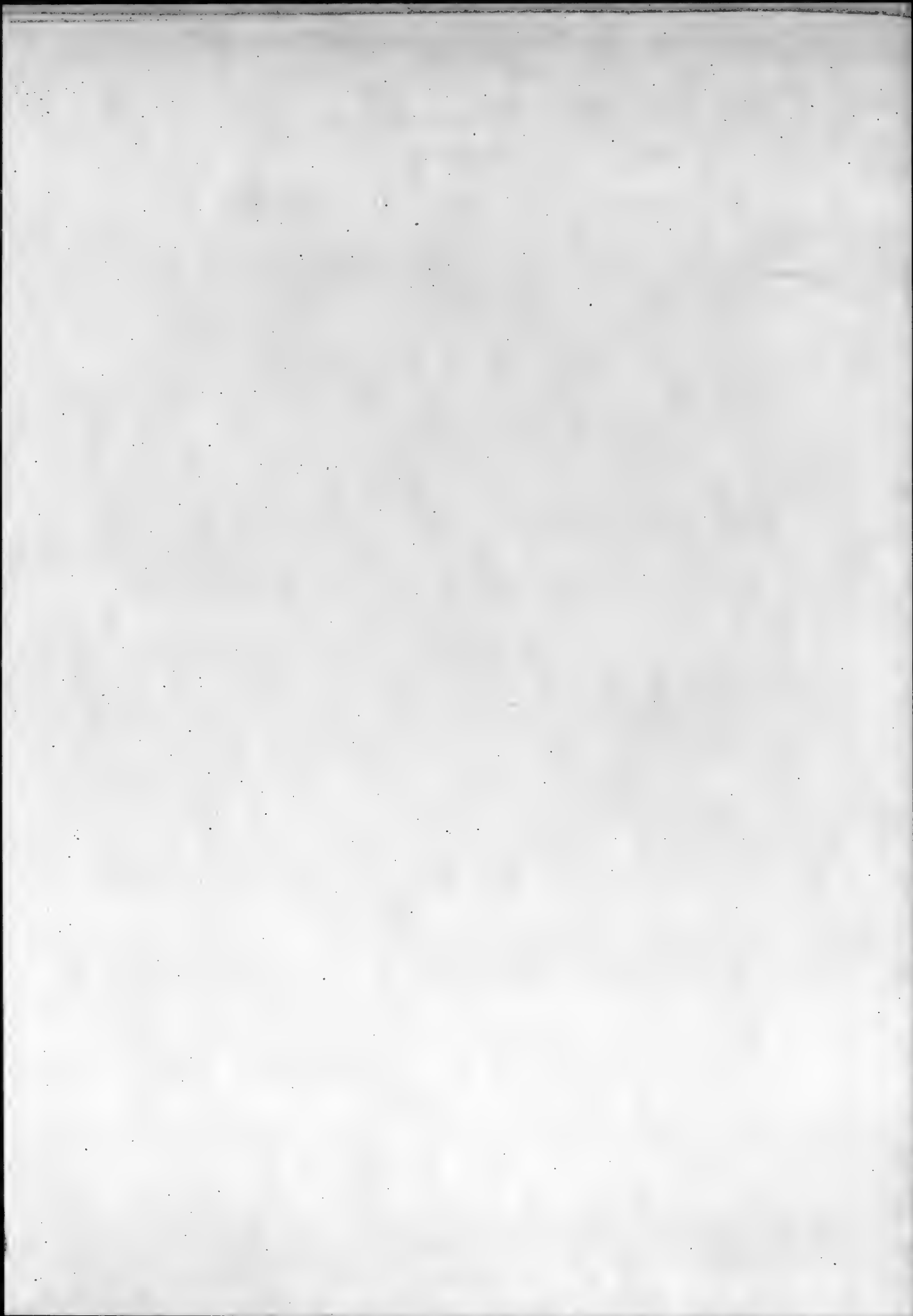
1. A series of dialkylalkoxyphenylthiophosphates and diethyl-4-thiocyanophenylthiophosphates, unreported in the literature, was synthesized in order to study their insecticidal properties.
2. A study of the insecticidal properties of the compounds obtained showed that they all were less active than diethyl-4-nitrophenylthiophosphate.

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Received April 21, 1953.

• See Consultants Bureau Translation, page 441.



## INVESTIGATION OF FURANE COMPOUNDS

### IV. EXPERIMENTS ON THE ASYMMETRIC SYNTHESIS OF SPIRANES AND TETRAHYDROFURANE ALCOHOLS

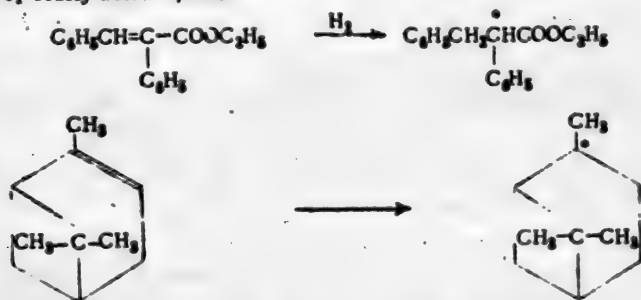
A. A. Ponomarev and V. V. Zelenkova

Among the recent investigations of asymmetric syntheses, those based upon the asymmetrizing action of optically active quartz crystals have attracted attention.

Ostromyslensky [1] first discovered the predominating separation of one of the optically active forms from a solution of the racemate under the influence of an optically active crystal of another organic substance. This was the start of further investigations on the asymmetrizing actions of crystals, in particular, asymmetric syntheses of various organic compounds with reactions conducted with the aid of catalysts deposited upon optically active quartz. Thus, Schwab and coworkers [2] conducted experiments upon the cleavage of secondary butyl alcohols with Cu, Ni, and Pt catalysts using an optically active form of quartz as the carrier. The undecomposed alcohol rotated the plane of polarization ( $\alpha_D$  0.1-0.13°) i.e., a preferential cleavage of one of the optically active forms occurred on the catalyst surface. Somewhat later Stankevich [3] repeated and widened the experiments of Schwab and attained an increase in the angle of rotation of the undecomposed alcohol to  $\alpha_D$  0.25°.

Both of the above investigations are examples of destructive asymmetric synthesis, i.e., the racemate is enriched by one optically active form because of the preferential decomposition of the second form.

The problem of asymmetric synthesis as a whole, and in particular of catalysis with the participation of a dissymmetric crystalline lattice was subjected to a thorough theoretical and experimental examination in the investigations of A. P. Terentyev, E. I. Klabunovsky, and V. V. Patrikeev [4,5]. The above cited authors, in addition to further developing the destructive asymmetric synthesis, also successfully solved the problem of "synthetically absolute asymmetric synthesis". In particular, optically active forms of hydrogenated compounds were obtained by the hydrogenation of ethyl  $\alpha$ -phenylcinnamate and  $\alpha$ -pinene (optically inactive compounds) with a nickel catalyst deposited upon optically active quartz:



The maximum values of the rotation of the plane of polarization were +0.05° and -0.09°, respectively. The hydrogenation experiments were conducted at usual pressure and 135° in decalin solution. The above investigation stimulated the idea of using a nickel quartz catalyst for the hydrogenation of furane alcohols.

As we know, spiranes are formed in addition to the corresponding tetrahydro alcohols by the catalytic hydrogenation of certain furane carbonyl compounds and alcohols. For example, 1,6-dioxaspiro-(4,4)-nonane and tetrahydrofurylpropanol are formed by the hydrogenation of furylpropanol.



Homologs of dioxaspiro-nonane were formed in an analogous manner by the hydrogenation of other  $\gamma$ -furyalk-nols. The mechanism for the formation of the spiranes was discussed in the previous communication [10]. The stereochemistry of these bicyclic products has not been studied up to now, even though it is of undoubted interest, especially in regard to the simplest of the spiranes of this type, 1,6-dioxaspiro-nonane. Because of the presence of two hetero atoms and the mutually perpendicular distribution of the rings, the latter must exist in two optically active forms.



which is a very clear example of an optically active molecule not containing asymmetric carbon atoms.

The methyl homolog of this spirane arises by the hydrogenation of furylbutanol; tetrahydrofurylbutanol is formed at the same time:



Both of the products obtained already possess two asymmetric carbon atoms, and therefore, must each exist in the form of two racemates under the usual conditions.

In order to prove experimentally the optical activity of 1,6-dioxaspiro-(4,4) nonane, experiments on the asymmetric synthesis of this compound with a nickel quartz catalyst were conducted. In addition, the optical activity of the simultaneously obtained tetrahydrofurylpropanol, as well as that of the methyl homolog of the spiro-nonane and tetrahydrofurane alcohol, obtained under analogous conditions, was proved by means of polarimetric measurement.

The hydrogenation experiments, in contrast to those of A. P. Terentyev, were conducted under pressures of 140-150 atm., which were necessary conditions for the formation of spiranes in satisfactory yields. Hydrogenation with simultaneous ring closure (for the formation of the spirane) also was a new type of reaction in comparison to the previous investigations on the asymmetric synthesis.

The results of the determination of the optical activity of the spiranes and tetrahydrofurane alcohols obtained by the use of nickel upon optically active quartz as a catalyst are summarized in Table 1.

Therefore, the existence of optical antipodes of spiranes and tetrahydrofurane alcohols can be considered experimentally proved.

## EXPERIMENTAL

The catalyst, nickel on optically active quartz, was prepared by the precipitation of basic nickel carbonate on the quartz followed by reduction to metallic nickel with hydrogen. For example, 4.9 g of optically active quartz pulverized in an agate mortar, was ground for 15-20 minutes with a solution of 5.8 g of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 8 ml of water. The homogenous mixture (homogeneity was kept by continuous efficient stirring) was added dropwise to a solution of 3.4 g of  $(\text{NH}_4)_2\text{CO}_3$  in 20 ml of water. A thick mass with equally distributed particles of quartz and basic nickel carbonate was obtained. The precipitate was filtered, washed twice with small amounts of water, dried in a drying cabinet at 105-115°, and was carefully stored after being ground with glass rod. Weight of the catalyst obtained, 7.11 g. The ratio of the weight of the nickel carbonate to that of the carrier was 1:2.2. Directly before the hydrogenation, the catalyst was reduced with hydrogen at 300-320° until the formation of water stopped, and was cooled by a stream of  $\text{CO}_2$ .

The given procedure is usually applied for the preparation of nickel on kieselguhr [6].

The samples of optically active quartz were kindly donated by V. S. Vasilev, the head of the Chair of Petrography and Mineralogy of the author's university.

The furane alcohols used for the experiments on asymmetric synthesis were prepared by the hydrogenation of the corresponding furane carbonyl compounds with a copper-chromite catalyst at 120° and 90-120 atm of hydrogen pressure.

TABLE 1

Optical Activity of Several Hydrogenation Products of Furylpropanol and Furylbutanol Obtained with Nickel on Optically Active Quartz.

Starting substance	Hydrogenation products	Carrier	Tube length (in dm)	$\alpha_D^\circ$	Average error of determination F*
1-( $\alpha$ -Furyl)-propanol	1,6-Dioxaspiro-(4,4)-nonane	l-quartz	1.9	-0.066	$\pm 0.005$
	1,6-Dioxaspiro-(4,4)-nonane	l-quartz	1	-0.03	$\pm 0.004$
	1-Tetrahydrofurylpropanol-3	l-quartz	2	-0.04	$\pm 0.005$
	1,6-Dioxaspiro-(4,4)-nonane	d-quartz	2	+0.06	$\pm 0.003$
	1-Tetrahydrofurylpropanol-3	d-quartz	1.9	+0.04	$\pm 0.004$
1-( $\alpha$ -Furyl)-butanol	2-Methyl-1,6-dioxaspiro-(4,4)-nonane	l-quartz	2	-0.02	$\pm 0.004$
	1-Tetrahydrofurylbutanol-3	l-quartz	2	+0.03	$\pm 0.004$
	2-Methyl-1,6-dioxaspiro-(4,4)-nonane	d-quartz	1.9	+0.02	$\pm 0.003$
	1-Tetrahydrofurylbutanol-3	d-quartz	1.9	-0.04	$\pm 0.002$

Furyl propanol was obtained from furylacrolein; it is an almost colorless liquid with b.p. 98-100° at 13mm,  $n_D^{20}$  1.4752 (literature data: b.p. 98° at 10 mm,  $n_D^{25}$  1.4760) [7]. 1-Furylbutanol-3 was obtained from furylacetone; it was a yellowish liquid with b.p. 126-129° at 52 mm,  $n_D^{25}$  1.4748 (literature data: b.p. 126-128° at 55 mm,  $n_D^{25}$  1.4744) [8].

The existence of optical activity for both furane alcohols was established by polarimetric measurement.

Experiments on asymmetric synthesis with nickel quartz catalyst were conducted at 120° and an initial pressure of 135-150 atm of hydrogen in absolute alcohol solution. Upon exhaustive hydrogenation under these conditions, 1-1.3 moles of hydrogen were absorbed per mole of alcohol used for the experiment. At the end of hydrogenation, the catalyst was filtered, and the hydrogenizate (after removal of the alcohol) was subjected to vacuum distillation. By redistillation, narrow fractions were isolated which corresponded to the spiranes and tetrahydrofurane alcohols in boiling point and refractive indices (Table 2).

The total yield of the spirane and tetrahydrofurane alcohol was 71.5% for furylpropanol with l-quartz, 48.2% with d-quartz; the corresponding figures for furylbutanol were 87.4% and 85.2%.

Measurement of the optical activity was conducted with a Lippikh polarimeter (Firm of Schmidt and Gench). All of the measurements were effected at 6 to 25 readings; 2-3 series of measurements were made with the same substance. The determination of the zero point of the polarimeter, as a rule, was conducted with an empty tube before and after the measurement with the substance.

As an example, an experiment on the hydrogenation of furylpropanol with nickel on d-quartz, and the polarimetric measurements of the products obtained are given below.

Hydrogenation of 1-( $\alpha$ -furyl)-propanol with nickel on d-quartz. 70 g of furylpropanol was dissolved in 80 ml of absolute alcohol and hydrogenated in the presence of 15.5 g of nickel on d-quartz (ratio of weight of the nickel carbonate precipitate to that of the carrier, 1:12) at 120° with an initial pressure of 142 atm of hydrogen. 14 liters of hydrogen were absorbed within 4 hours, i.e., 1.2 moles of hydrogen per mole of alcohol. The catalyst was filtered, the alcohol removed, and the residue subjected to vacuum distillation. The distillate was separated into two fractions by redistillation.

I. Dioxaspiro-nonane, b.p. 81-82° at 60 mm,  $n_D^{20}$  1.4478, weight 13.03 g (18.6%). II. Tetrahydrofurylpropanol, b.p. 141-144° at 60 mm,  $n_D^{20}$  1.4592, weight 21.07 g (29.6%).

The fractions were used for the measurement of the optical activity of both products (Tables 3 and 4).

\*The average error of determination F was calculated according to the formula:

$$F = \sqrt{\frac{\sum (f_m^2)}{n(n-1)}}$$
 where  $f_m = m - M$  is the difference between the value of the rotation of the given and the arithmetic average,  $n$  is the number of measurements.



TABLE 2

Several Constants of Spiranes and Tetrahydrofuran Alcohols Obtained as Results of Experiments on Asymmetric Synthesis

Name of substance	Boiling point (in °)	$n_D^{25}$	Literature data [9]	
			b.p. (in °)	$n_D^{25}$
1,6-Dioxaspiro-(4,4)-nonane	83-84 (62 mm)	1.4464	81-82 (60 mm)	1.4465
	81-82 (60 mm)	1.4465		
1-( $\alpha$ -Tetrahydrofuryl) propanol-3	139-144 (58 mm)	1.4595	144 (60 mm)	1.4563
	141-144 (60 mm)	1.4580		
2-Methyl-1,6-dioxaspiro-(4,4)-nonane	77-78 (43 mm)	1.4410	80 (46 mm)	1.4412
	79-81 (46 mm)	1.4415		
1-( $\alpha$ -Tetrahydrofuryl)-butanol-3	128-130 (44 mm)	1.4570	145 (58 mm)	1.4541
	131-133 (48 mm)	1.4542		

TABLE 3

Measurement of the Optical Activity of 1,6-Dioxaspiro-(4,4)-nonane Obtained by the Hydrogenation of Furylpropanol with Nickel on d-Quartz.

Zero point with 2 dm tube	Measurement with tube filled with the spirane	Zero point of the tube after measurement
0.19	0.25	0.20
0.18	0.25	0.20
0.18	0.26	0.21
0.20	0.25	0.19
0.17	0.25	0.20
0.16	0.25	0.20
0.19	0.24	0.22
0.17	0.26	0.21
0.17	0.24	0.22
0.20	0.26	0.20
0.16	0.26	—
0.16	0.26	—
0.18	—	—
0.17	—	—
0.18	—	—

Average of 15 readings 0.177°  
 $F \pm 0.003^\circ$

Average of 12 readings 0.251°  
 $F \pm 0.002^\circ$

Average of 10 readings 0.205°  
 $F \pm 0.003^\circ$

Average zero point  $0.191^\circ$ ;  $\alpha_D^{25} + 0.06^\circ$

TABLE 4

Measurement of the Optical Activity of 1-( $\alpha$ -Tetrahydrofuryl)-propanol-3 Obtained by the Hydrogenation of Furylpropanol with Nickel on d-Quartz.

Zero point with 2 dm tube	Measurement with tube filled with tetrahydrofuryl propanol	Zero point of the tube after measurement
0.23	0.25	0.21
0.23	0.24	0.24
0.23	0.28	0.24
0.23	0.26	0.23
0.24	0.26	0.23
0.22	0.25	0.24
0.21	0.26	0.22
0.21	0.26	0.23
0.23	0.26	0.21
0.23	0.26	0.23
0.22	—	—
0.22	—	—
0.22	—	—
0.21	—	—
0.24	—	—

Average of 15 readings 0.224°  
 $F \pm 0.002^\circ$

Average of 10 readings 0.268°  
 $F \pm 0.004^\circ$

Average of 10 readings 0.228°  
 $F \pm 0.004^\circ$

Average zero point  $0.226^\circ$ ;  $\alpha_D^{25} + 0.042^\circ$

## SUMMARY

1. An asymmetric synthesis of 1,6-dioxaspiro-nonane was accomplished which proved, experimentally, the theoretical belief of the stereoisomerism of this compound.

2. The fact of asymmetric synthesis with a nickel catalyst deposited on  $\bar{l}$ - and  $\bar{d}$ -quartz was established, which was also accompanied by the intramolecular cyclization (formation of spiranes).

At the same time, the practical possibility to realize an asymmetric synthesis in the presence of the above catalyst at high pressures and temperature was shown on the example of the hydrogenation of furylpropanol and furylbutanol.

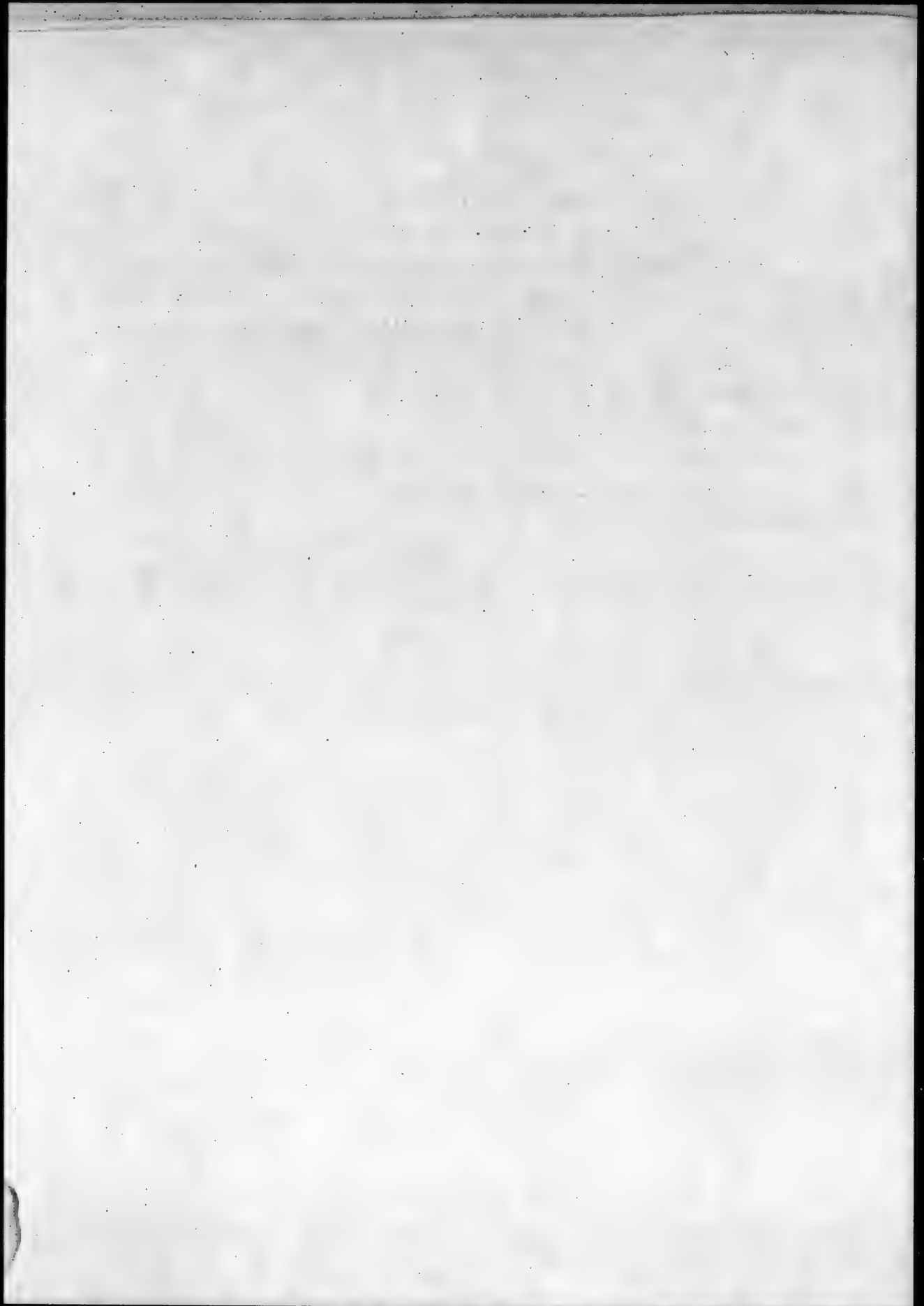
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Received January 6, 1953.

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\* See Consultants Bureau Translation, page 1493.



SYNTHESIS  
OF AROMATIC ORGANOELEMENTAL COMPOUNDS  
BY THE REACTION OF ARYL SILANES WITH ALUMINUM CHLORIDE  
AND HALIDES OF VARIOUS ELEMENTS  
I. ORGANOPHOSPHOROUS COMPOUNDS

A. Ya. Yakubovich and G. V. Motsarev

Several methods are known for the preparation of aryl dichlorophosphines. Thus, they can be prepared by passing vapors of aromatic hydrocarbons with phosphorus trichloride through an incandescent porcelain or glass tube [1]. Another method for the preparation of these compounds is based upon the use of organo mercury compounds. For example,  $C_6H_5PCl_2$  can be obtained by the reaction between  $(C_6H_5)_2Hg$  and  $PCl_3$  [2].

The most satisfactory of all of the known methods of synthesis of aryl dichlorophosphines is their preparation by the reaction of aromatic halogen derivatives (benzene, chloro- and bromobenzene, toluene, xylene, and others) with phosphorus trichloride in the presence of anhydrous aluminum chloride as a catalyst [3-7]. Nevertheless, this method is not free of shortcomings, the main one of which is the formation of several isomers during the reaction.

Therefore, the known methods for the preparation of aryl dichlorophosphines show that these compounds are still relatively poorly available substances, without even considering their derivatives containing various substituents in the aromatic radical.

Because the authors previously showed that dichlorophosphines were formed by the action of  $PCl_3$  upon the product of the reaction between phenyl trichlorosilane and anhydrous  $AlCl_3$  [8], a detailed investigation of this reaction was undertaken in order to determine the possibility and the conditions for the synthesis of various aromatic organo phosphorus compounds by this method. The present communication reports on the results of the investigation on the synthesis of aromatic dichlorophosphines and their derivatives with various substituents in the aromatic ring.

The method reported below for the preparation of aryl dichlorophosphines and their derivatives is based on the use of aromatic silanes of the general formula  $(C_6H_5-nX_n)_mSiCl_{4-m}$  (where  $m =$  from 1 to 4) which are reacted with phosphorus trichloride in the presence of anhydrous aluminum chloride.

The formation of aromatic organo phosphorus compounds with this reaction occurs because the aromatic silanes and their derivatives (with substituents in the aromatic ring), as was previously shown by the authors in one of the previous communications [8], undergo a cleavage of the  $C-Si$  bond under the influence of aluminum chloride with the formation of the corresponding organo-aluminum compounds of the type  $ArAlCl_2$ . Such compounds react with  $PCl_3$  as a result of which the corresponding aromatic aryl dichlorophosphines are obtained.

This course of the reaction may be represented in a general form by the following series of equations:



Where  $X = H, Cl, Br, I, R$ , etc.,  $m =$  From 1 to 4,  $n =$  From 0 to 5

The phosphorus trichloride can enter into reaction in two ways: either simultaneously with the aromatic silane and aluminum chloride, which leads to the reaction of  $PCl_3$  with the organo-aluminum compound at the moment of its formation; or after the aromatic silane is decomposed by the aluminum chloride, followed by the

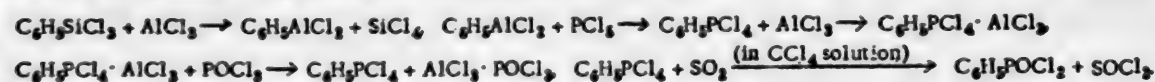
removal of the silicon tetrachloride from the reaction mass. In a preparative relation the first course is more convenient without even considering that it leads to the preparation of aryl dichlorophosphines with somewhat higher yields.

In order to prepare aryl dichlorophosphines by this method, the aromatic silane, for example an aryl trichlorosilane, is mixed with phosphorus trichloride and aluminum chloride in a ratio of  $\text{ArSiCl}_3 : \text{PCl}_3 : \text{AlCl}_3 = 1.0 : 1.0 : 1.1$ . Even the simple mixing of the mixture of the above reagents leads to the heating up of the mixture and a gradual solution of the aluminum chloride. With further heating of the reaction mixture to  $80^\circ$ , an almost complete solution of the aluminum chloride and the separation of the reaction mixture into two layers occurs: the upper one, colorless, is silicon tetrachloride, and the lower one, oily light brown. The latter is the complex compound of aryl dichlorophosphine with aluminum chloride.

If phosphorus oxychloride acts upon this complex after the removal of the silicon tetrachloride, the aryl dichlorophosphine is displaced from it, and a new complex  $\text{POCl}_3 \cdot \text{AlCl}_3$  is formed which makes the isolation of the aryl dichlorophosphine in pure form possible. In this manner, phenyl-, p-chlorophenyl, p-bromophenyl, and p-tolylphenyl-dichlorophosphines were isolated in good yields.

The above examples show that the method reported above can serve as a convenient general method for the synthesis of primary dichlorophosphines and their various derivatives.

With the aid of the organo aluminum compounds, formed as intermediate products by the reaction of phenylchlorosilanes with  $\text{AlCl}_3$ , not only can the aryl dichlorophosphines be prepared, but also the acid chlorides of the aryl phosphinic acids. This reaction was studied by means of the reaction of phenyltrichlorosilane with  $\text{AlCl}_3$  and phosphorus pentachloride. The formation of phenylphosphenyl chloride occurs in this case according to the scheme:



It is interesting to mention that phosphorus oxychloride in contrast to phosphorus pentachloride, does not react with phenyl aluminum dichloride.

## EXPERIMENTAL

### I. Phenyl Dichlorophosphine $\text{C}_6\text{H}_5\text{PCl}_2$

1. Preparation from  $\text{C}_6\text{H}_5\text{SiCl}_3$ . a)  $\text{PCl}_3$  was introduced into the reaction simultaneously with the  $\text{C}_6\text{H}_5\text{SiCl}_3$  and  $\text{AlCl}_3$ . 100.0 g of phenyltrichlorosilane, 69.3 g of freshly sublimed anhydrous aluminum chloride, and 65.0 g of phosphorus trichloride were placed into a round-bottomed flask connected to a condenser and a trap cooled with an acetone carbon dioxide mixture ( $-40^\circ$ ), and fitted with a calcium chloride tube. The mixture was heated for 2 hours on the water bath at  $80^\circ$ , and then the silicon tetrachloride was removed (by shutting off the reflux condenser and putting on the vacuum). 75.5 g of silicon tetrachloride (yield 94.4% of the theoretical) was obtained in the receiver. 85.8 g of phosphorus oxychloride was added gradually to the hot oil-like residue in the flask after the removal of the  $\text{SiCl}_4$ , which led to the formation of a grainy precipitate. The precipitate was treated with several portions of petroleum ether, the extracts were combined, the petroleum ether was removed, and the residue vacuum distilled. Vacuum distillation resulted in 70.0 g (83.4%) of phenyldichlorophosphine in the form of a strongly refractive, light yellow liquid with a b.p. of  $140-141^\circ$  (57 mm),  $d_{20}^{25} 1.3180$ , which fumed in the air and possessed a sharp unpleasant odor (literature data: b.p.  $222, 140-142^\circ$  (57 mm)  $d_{20}^{25} 1.319$  [2]).

0.2083, 0.2004 g substance. In 25 ml 0.5 N KOH: 22.9, 21.95 ml 0.1 N  $\text{AgNO}_3$ . Found%: hydrolyzable Cl 39.02, 38.94.  $\text{C}_6\text{H}_5\text{PCl}_2$ . Calculated %: Cl 39.66.

b)  $\text{PCl}_3$  was introduced into the reaction after the cleavage of  $\text{C}_6\text{H}_5\text{SiCl}_3$  by aluminum chloride and after the removal of  $\text{SiCl}_4$ . 20.0 g of phenyltrichlorosilane and 12.9 g of freshly sublimed anhydrous aluminum chloride were placed into a round-bottomed flask fitted to a calcium chloride tube and connected in the same manner as in the previous experiment, with a reflux condenser and a receiver. Upon mixing the reagents, the reaction mass turned red. In order to accelerate the reaction, the mixture was heated at  $70-80^\circ$  with the simultaneous removal of the silicon tetrachloride formed, by connecting the entire system to a vacuum.

13.9 g of  $\text{SiCl}_4$  or 87.0% were obtained in the receiver. 13.0 g of phosphorus trichloride was added gradually to the semi-solid brown residue after the removal of the  $\text{SiCl}_4$ . After the addition of all of the  $\text{PCl}_3$ , the mixture became liquid. The mixture was heated for 1 hour at  $80-90^\circ$ , and then 17.2 g of phosphorus oxychloride was added gradually to it. The further isolation of phenyldichlorosilane was conducted in analogous manner to that



reported above. 12.8 g of phenyldichlorophosphine with b.p. 140° (56 mm) was obtained. Yield, 76.0% of the theoretical based upon the starting phenyltrichlorosilane.

0.2321, 0.1972 g substance in 25 ml 0.5 N KOH: 25.6, 21.55 ml 0.1 N AgNO<sub>3</sub>. Found %: Hydrolyzable Cl 39.14, 36.83. C<sub>6</sub>H<sub>5</sub>PCl<sub>2</sub>. Calculated %: Cl 39.66.

2. Preparation from (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiCl<sub>2</sub>. A mixture consisting of 10.0 g diphenyldichlorosilane, 11.6 g of freshly sublimed aluminum chloride, and 11.0 g of phosphorus trichloride was heated for 3 hours on the water bath at 80°. Silicon tetrachloride was distilled from the reaction mass, which had separated into layers (6.2 g or 92.7% of the theoretical), and 14.3 g of phosphorus oxychloride was slowly added to the residue. The phenyldichlorophosphine was then isolated by the above reported method. 11.3 g of phenyldichlorophosphine with b.p. 139-139° (55 mm) was obtained. (Yield, 80.4% of the theoretical).

0.1826, 0.2233 g substance in 25 ml 0.5 N KOH: 20.0, 24.6 ml 0.1 N AgNO<sub>3</sub>. Found %: Hydrolyzable Cl 38.91, 39.10. C<sub>6</sub>H<sub>5</sub>PCl<sub>2</sub>. Calculated %: Cl 39.66.

## II. p-Chlorophenyldichlorophosphine p-ClC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub>.

10.0 g of p-chlorophenyltrichlorosilane, obtained, either as the result of the reaction of p-ClC<sub>6</sub>H<sub>4</sub>MgBr with SiCl<sub>4</sub> [9], or by the chlorination of phenyltrichlorosilane in the presence of a catalyst [10], was mixed with 6.0 g of freshly sublimed aluminum chloride, and 5.7 g of phosphorus trichloride. The mixture was heated for 2 hours on the water bath at 80°; the silicon tetrachloride was then removed (6.3 g or 90.7%), 7.0 g of phosphorus oxychloride was gradually added to the residue.

The isolation of p-chlorophenyldichlorophosphine was effected by a method analogous to that reported for the isolation of phenyldichlorophosphine. 6.6 g of p-chlorophenyldichlorophosphine was obtained in the form of a colorless oil-like liquid with an unpleasant odor and b.p. of 252-253°, d<sub>20</sub><sup>25</sup> 1.4203. (Literature data: b.p. 253-255°, d<sub>20</sub><sup>25</sup> 1.425 [5]). Yield, 77.4% of the theoretical based on p-chlorophenyltrichlorosilane.

0.2381, 0.2452 g substance in 25 ml 0.5 N KOH: 21.9, 22.6 ml 0.1 N AgNO<sub>3</sub>. 0.1420, 0.1137 g substance; 0.2823, 0.2255 g AgCl (Carius). Found %: Hydrolyzable Cl 32.67, 32.74; Total Cl 49.21, 49.09. ClC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub>. Calculated %: Hydrolyzable Cl 33.25; Total Cl 49.88.

## III. p-Bromophenyldichlorophosphine p-BrC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub>.

10.0 g of p-bromophenyltrichlorosilane, obtained either by means of the organo magnesium synthesis by the reaction of p-BrC<sub>6</sub>H<sub>4</sub>MgBr with SiCl<sub>4</sub> [9], or by the bromination of phenyltrichlorosilane in the presence of a catalyst [11], was mixed with 5.0 g of freshly sublimed aluminum chloride and 4.7 g of phosphorus trichloride. The mixture was heated for 2 hours on the water bath at 80°; the silicon tetrachloride was then removed (5.2 g or 89.6%), and 5.9 g of phosphorus oxychloride was added gradually to the residue. The isolation of p-bromophenyldichlorophosphine was effected by the same method (see the previous experiment). 6.4 g of p-bromophenyldichlorophosphine was obtained in the form of a colorless, highly refractive, thick liquid with a b.p. of 270°, d<sub>20</sub><sup>25</sup> 1.6861. (Literature data: 271-272°, d<sub>20</sub><sup>25</sup> 1.6895 [5]). Yield 72.6%, based on the p-bromophenyltrichlorosilane used for the reaction.

0.2520, 0.2310 g substance in 25 ml 0.5 N KOH: 19.1, 17.6 ml 0.1 N AgNO<sub>3</sub>. Found %: Hydrolyzable Cl 26.91, 27.03. BrC<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub>. Calculated %: Hydrolyzable Cl 27.51.

-Upon treatment with water, p-bromophenylphosphinic acid was obtained which was analyzed for bromine content. 3 g of p-bromophenyldichlorophosphine was dropped into 10 ml of water. The precipitate which formed, was filtered and washed with cold water (3-5°). After recrystallizing it from aqueous alcohol, thin platelets with m.p. 142.3° were obtained, which corresponded to the melting point of p-bromophenylphosphinic acid (literature data: m.p. 143° [5]).

0.1276, 0.1451 g substance: 0.1067, 0.1220 g AgBr (Carius). Found %: Br 35.61, 35.82. BrC<sub>6</sub>H<sub>4</sub>P(OH)<sub>2</sub>. Calculated %: Br 36.19.

## IV. p-Tolyldichlorophosphine p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub>.

10.0 g p-tolyldichlorosilane, synthesized from p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>MgBr and SiCl<sub>4</sub>, was mixed with 6.5 g of freshly sublimed aluminum chloride and 6.1 g of phosphorus trichloride. The mixture was heated on the water bath for 2 hours at 80°; the silicon tetrachloride was then removed (7.0 g or 93.8%), and 7.5 g of phosphorus oxychloride was gradually added to the residue.

The subsequent isolation of p-tolyldichlorophosphine from the reaction mass was accomplished by the method reported above for other phosphines. 7.2 g of p-tolyldichlorophosphine (85.3%) was obtained in the form of a colorless, crystalline substance (platelets from ether) with m.p. 24.5°, b.p. 243-244° (literature b.p. 245°; m.p. 25° [4]).

0.2119, 0.2334 g substance in 25 ml 0.5 N KOH: 21.55, 23.65 ml 0.1 N AgNO<sub>3</sub>. Found %: Hydrolyzable Cl 36.11, 36.01. CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>PCl<sub>2</sub>. Calculated %: Hydrolyzable Cl 36.78.

**V. Reaction of Phenyltrichlorosilane with AlCl<sub>3</sub> and PCl<sub>5</sub>. Preparation of Phenylphosphoryl chloride C<sub>6</sub>H<sub>5</sub>POCl<sub>2</sub>.** 40.0 g of phenyltrichlorosilane was added with stirring to a mixture of 30.2 g of freshly sublimed aluminum chloride and 39.4 g of phosphorus pentachloride. Upon the addition of phenyltrichlorosilane, a noticeable evolution of heat occurred, and the reaction mass became red brown. Heating of the mixture for 2 hours at 80-85° led to almost complete disappearance of the solid phase and the formation of two layers: the upper layer was very mobile and colorless; the lower, brown, oil-like. In order to remove the silicon tetrachloride, the reaction mass was heated on the water bath in vacuum.

28.7 g of SiCl<sub>4</sub> (yield 89.6% of the theoretical) was obtained in the receiver cooled with acetone-carbon dioxide mixture (-40°). 38.2 g of phosphorus oxychloride was added to the cooled residue obtained after the removal of the silicon tetrachloride, which led to the formation of a precipitate. After the addition of all of the POCl<sub>3</sub>, the reaction mass was heated for 1 hour at 70°, 40.0 ml of carbon tetrachloride was added to it, and it was treated in the cold with dry sulfur dioxide until the evolution of heat stopped. The liquid part was separated from the solid grainy residue and subjected to fractionation. The main part of the CCl<sub>4</sub> in a mixture with SOCl<sub>2</sub> was distilled at atmospheric pressure, and the remainder and the POCl<sub>3</sub> was removed in vacuum. The residue after the removal of the solvents, was distilled from a metallic bath at usual pressure. The following fractions were collected: 1 with b.p. 193-199°-4.0 g, 2 with b.p. 200-250°-0.8 g, 3 with b.p. 250-259°-19.6 g. Fraction 1 was redistilled at ordinary pressure; 3.5 g of a liquid with b.p. 197-199° was obtained; it was phenyltrichlorosilane.

0.2374, 0.2462 g substance. in 25 ml 0.5 N alcoholic KOH: 33.2, 34.5 ml 0.1 N AgNO<sub>3</sub>. Found %: Hydrolyzable Cl 49.7, 49.8. C<sub>6</sub>H<sub>5</sub>SiCl<sub>3</sub>. Calculated %: Hydrolyzable Cl 50.3.

Fraction 3 was redistilled at ordinary pressure. 16.8 g of a liquid with b.p. 256-258° and d<sub>4</sub><sup>20</sup> 1.3700. Yield 45.6% of the theoretical.

0.2167, 0.2226 g substance in 25 ml 0.5 N KOH: 21.85, 22.55 ml 0.1 N AgNO<sub>3</sub>. Found %: Hydrolyzable Cl 35.84, 35.97. C<sub>6</sub>H<sub>5</sub>POCl<sub>2</sub>. Calculated %: Hydrolyzable Cl 36.41.

Therefore, fraction 3 was phenylphosphoryl chloride the constants of which were reported by Michaelis [2]: b.p. 258°, d<sub>4</sub><sup>20</sup> 1.375.

#### **VI. Reaction of Phenyltrichlorosilane with AlCl<sub>3</sub> and POCl<sub>3</sub>**

A mixture of 30.0 g of phenyltrichlorosilane and 20.7 g of freshly sublimed aluminum chloride was heated for 4 hours on the water bath at 80°. Toward the end of the heating, the reaction mixture acquired a red brown color and boiled violently. After cooling to 30°, 68.7 g of phosphorus oxychloride was added to it; the addition was accompanied by a noticeable heating up of the reaction mixture. At the end of the addition of the POCl<sub>3</sub>, the reaction mixture was heated for 1 hour at 80°, and the volatile products were removed from it in vacuum. About 50.0 g of a liquid was obtained in the receiver cooled with acetone carbon dioxide mixture (-40°), which yielded the following fractions upon distillation: 1 with b.p. 54-60°-14.2 g, 2 with b.p. 60-102°-2.6 g, 3 with b.p. 102-108°-31.2 g.

Fraction 1 represented silicon tetrachloride, with b.p. 56-57°, d<sub>4</sub><sup>20</sup> 1.4820.

Fraction 3 was redistilled at ordinary pressure. The main part distilled at 105-107°.

Found %: Cl 68.71, 69.02. POCl<sub>3</sub>. Calculated %: Cl 69.38.

Therefore, fraction 3 was phosphorus oxychloride.

The semi-solid residue, obtained after the distillation of the volatile products, was treated with several portions of petroleum ether, the extracts combined, the ether removed, and the residue distilled first at atmospheric pressure, and then in vacuum.

Upon distillation, 5.0 g of phosphorus oxychloride (b.p. 103-108°) and 10.0 g of a fraction with b.p. 196-199° (70-72° at 7 mm), which was unchanged phenyltrichlorosilane, were obtained. The residue after the

distillation had the form of thick oil-like liquid, which violently decomposed in water.

In another experiment, the treatment of the semi-solid residue after the removal of the volatile products, was with benzene instead of petroleum ether; however, the same results were obtained as in the previous experiment.

#### SUMMARY

1. Primary aryl chlorophosphines were formed in good yields by the reaction of phosphorous trichloride with an organoaluminum compound obtained by the reaction of aryl chlorosilanes with  $AlCl_3$ . Aryl dichlorosilanes containing substituents such as Cl, Br,  $CH_3$  in the ring can also be obtained in this manner.

2. Phosphorus pentachloride reacted with phenyltrichlorosilane and  $AlCl_3$  to form phenyltetrachlorophosphine which was readily converted to phenylphosphoryl chloride. In contrast to  $PCl_5$ , phosphorus oxychloride did not give compounds with a C-P bond with an analogous reaction.

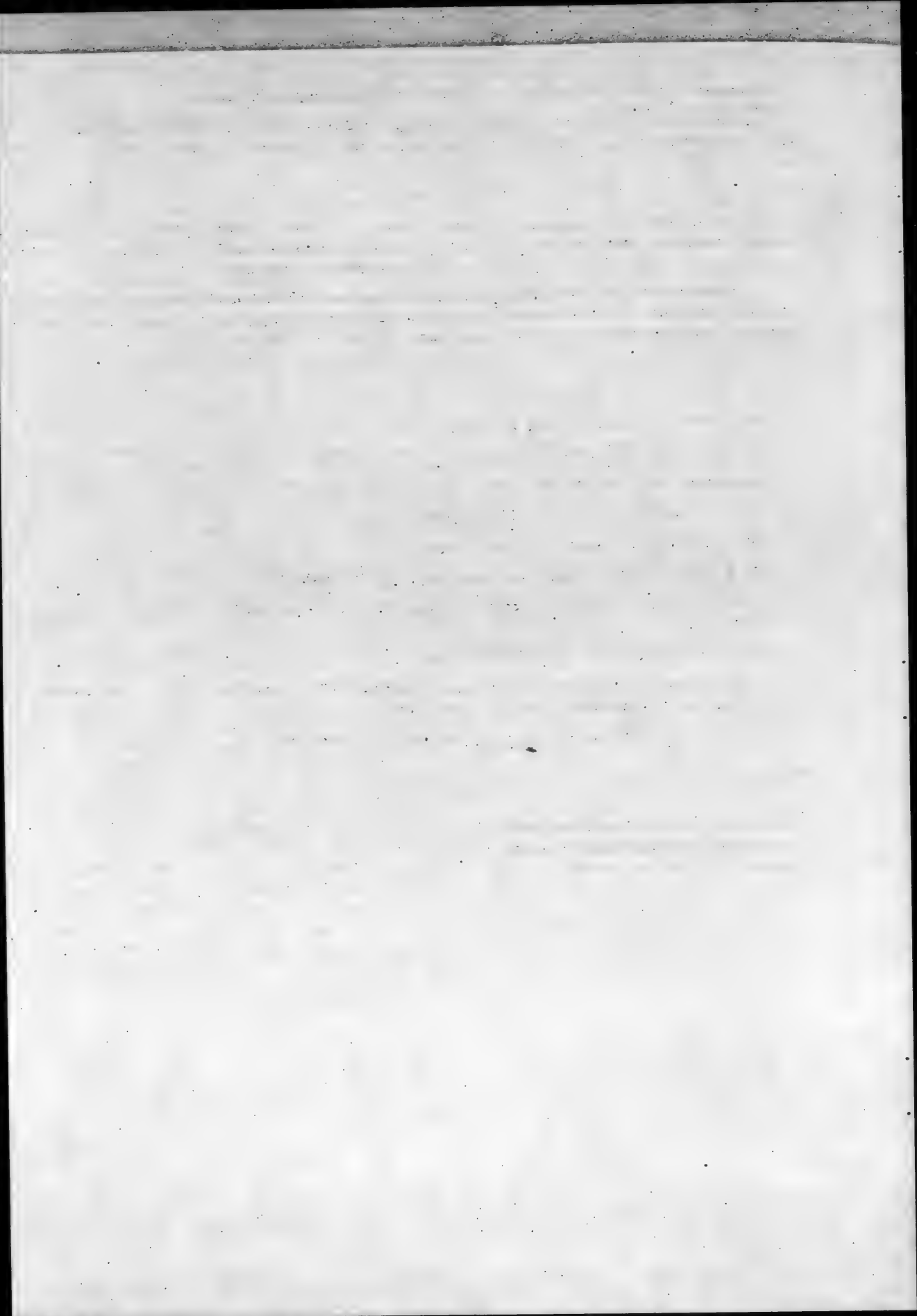
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Received February 21, 1953.

\* See Consultants Bureau Translation, page 1111.

\*\* See Consultants Bureau Translation, page 421.

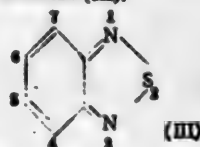
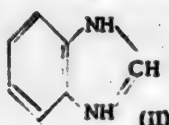
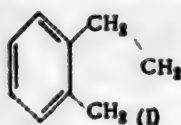


## NITRATION OF PLAZTHIOL

L. S. Efros and R. M. Levit

Generalizing the literature data upon the appearance of disruption of equalization of bonds in benzene rings entering into the composition of molecules with condensed nuclei, it can be concluded that three types of this phenomena are conceivable and exist in practice, depending on the degree of affinity of the adjacent ring to  $\pi$ -electrons.

In the first case, the adjacent ring repels  $\pi$ -electrons of the benzene ring from itself, and decreases the  $\pi$ -electron density of bonds common for both rings. Hydrindin (I) can serve as an example of a compound of this type [1]. In the second case, the adjacent ring possesses approximately the same affinity to the electrons as the benzene ring; characteristic compounds of this type are naphthalene, and as the authors showed [2] benzimidazole (II). Finally, in the case where the adjacent ring possesses a noticeably greater affinity for the electrons than benzene, there is a third type of disruption of the equalization of the bonds; plazthiol is a graphic example of such a compound; measurement of the interatomic distance of which [3] shows that it has the structure (III).



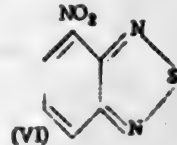
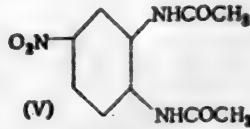
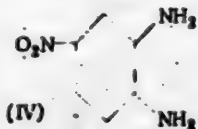
The disruption of equalization of the bonds in the benzene ring of imidazole, shown in formula (II) was found by studying the chemical properties of this compound [2]. On the other hand, a series of generalities in chemical behavior of substances with imidazole rings could be predicted using this representation of the phenomenon [4, 5].

It seemed of interest to proceed in another manner in the case of plazthiol, and to predict certain chemical properties of this substance, knowing its fine structure on the basis of the measurement of the interatomic distances. Thus, it was clear that in contrast to benzimidazole (II), the nitrogen atom in plazthiol (III) must cause a partial positive charge in positions 5 and 6, because of which the nitration of this compound should lead to the entrance of the substituent predominantly into positions 4 and 7.

Meanwhile, A. M. Khaletsky and V. G. Pesin [6] in a recently-published paper on the study of the nitration of plazthiol, stated that the product obtained by them was a 5-nitro derivative. They proved this structure by synthesizing this product from 4-nitro-1,2-phenylenediamine (IV) and thionyl chloride. Diamine (IV) they obtained by the acid hydrolysis of 4-nitro-1,2-diacytyldiaminobenzene (V).

Since it is known that, mainly, cyclization with the formation of 5-nitro-2-methylbenzimidazole occurs upon acid hydrolysis of compound (V) [7], and only traces of diamine (IV) are obtained, and since the conclusions on the structure of nitroplazthiol are based on these experiments and are in opposition to the conclusions from the above-theoretical views, it was decided to clarify this problem.

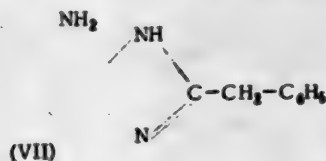
4-Nitro-1,2-phenylene diamine (IV) and 3-nitro-1,2-phenylenediamine, isomeric with it, were obtained in chemically pure form by known methods, partial reduction of 2,4-dinitroaniline and 2,6-dinitroaniline which was obtained by the authors. Upon treating 3-nitro-1,2-phenylenediamine with thionyl chloride under conditions reported by A. M. Khaletsky and V. G. Pesin, 4-nitroplazthiol (VI) was obtained which was identical with the nitration product of plazthiol:





It is interesting that 4-nitrophenylenediamine (IV) only reacts weakly with thionyl chloride in an analogous manner, which is readily explained by the electrophilic effect of the nitro group, which hinders the closing of the piazthiol ring.

For the final proof of the structure of the nitration product of piazthiol, this product was reduced with zinc and hydrochloric acid. The piazthiol ring was completely destroyed, and consecutive triaminobenzene hydrochloride was isolated from the reaction mass with a good yield. The previously reported [5] 4-amino-2-benzylbenzimidazole (VII) was obtained from it by condensation with phenylacetic acid:



Both of these products were identified against those obtained by the usual methods reported in the literature.

Therefore, the theoretical prognosis on the direction of the nitration of piazthiol, which was derived from a representation of the disruption of the equality of the bonds in its benzene ring, was completely proved.

The nitration of piazthiol followed by reduction of this compound occurring with the disruption of the heterocycle can be recommended as a method for the preparation of consecutive triaminobenzene since this product is synthesized with comparative difficulty by methods reported in the literature.

## EXPERIMENTAL

### Preparation of Piazthiol

50 g of o-phenylenediamine, 800 ml of toluene, and 150 g of thionyl chloride were placed in a flask equipped with a reflux condenser and calcium chloride tube. The mixture was heated for 12 hours on an oil bath. The toluene was then distilled from the flask by means of a herringbone dephlegmator, and the crude reaction product was subjected to vacuum distillation for final purification. Piazthiol distilled at 79-80° at 5 mm. 54.5 (86.5%), of piazthiol was obtained in the form of a crystalline substance melting at 42-44°.

### Preparation of 4-nitropiazthiol (According to Khaletsky and Pesin's method)

20 g of piazthiol and 56 ml of concentrated sulfuric acid (d 1.84) were placed into a flask equipped with a stirrer. A nitration mixture consisting of 12 ml of nitric acid (d 1.4) and 18 ml of concentrated sulfuric acid was added slowly from a dropping funnel. The nitration was conducted at 0°. At the end of the nitration, the reaction mixture was kept 0.5 hours at room temperature, and then poured on ice. A light yellow precipitate formed which was filtered and washed with cold water to a neutral reaction. The light yellow substance obtained after recrystallization from alcohol, melted at 107°. 25.5 g of nitropiazthiol (90.5%) was obtained.

### Preparation of 4-Nitropiazthiol from 1-Nitro-2,3-diaminobenzene.

1 g of 1-nitro-2,3-diaminobenzene with m.p. 156° obtained in the usual manner from 2,6-dinitroaniline, 30 ml of absolute dry toluene, and 2 g of thionyl chloride were placed in a flask equipped with a reflux condenser and a calcium chloride tube. The mixture was heated for 6 hours on an oil bath, filtered and poured into a crystallizer. 0.8 g of a light yellow substance (67.8%) with m.p. 107-108° was obtained upon recrystallization from water.

### Attempts to prepare 5-Nitropiazthiol from 1-Nitro-3,4-diaminobenzene

2 g of 1-nitro-3,4-diaminobenzene, m.p. 197-198° obtained in the usual manner from 2,4-dinitroaniline, 40 ml absolute dry toluene, and 4 g of thionyl chloride were placed into a flask equipped with a reflux condenser and a calcium chloride tube. The mixture was heated for 6 hours, filtered, and poured into a crystallizer. Upon evaporation of the toluene, a brown crystalline substance was obtained. After recrystallization from toluene, dark red crystals with m.p. 197° were obtained, i.e., the starting product. The synthesis was conducted with a double quantity of thionyl chloride and gave the same results.

### Preparation of 1,2,3-Triaminobenzene from 4-Nitroplazthiol

2.4 g of 4-nitropiazthiol was dissolved in 100 ml of hot water with 30 ml of concentrated hydrochloric acid. 12 g of zinc dust was added to the solution as rapidly as possible; a reduction occurred with a violent evolution of hydrogen sulfide. The solution obtained was filtered from impurities, 1,2,3-triaminobenzene dihydrochloride was obtained by the addition of 25 ml of concentrated hydrochloric acid in the form of long, thin needles. The salt was separated, dissolved in 20 ml of water, and the solution was shaken in the cold with activated carbon, filtered and colorless needles of the same salt of triaminobenzene were formed by the addition of concentrated hydrochloric acid. Yield, 1.8 g which was 67% of the theoretical amount

Upon condensation with phenylacetic acid [5], 4-amino-2-benzylbenzimidazole (VII) was obtained, whose salt melted at 242-248°, the base at 154°.

## SUMMARY

1. The 4-nitro derivative was formed upon the nitration of plazhiol in complete agreement with developed theoretical principles and in contrast to the literature data.
2. The nitration of plazhiol, followed by the reduction of the product which occurred with the disruption of the heterocycle, is a convenient method for the synthesis of vicinal triaminobenzene.

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Received May 20, 1953.

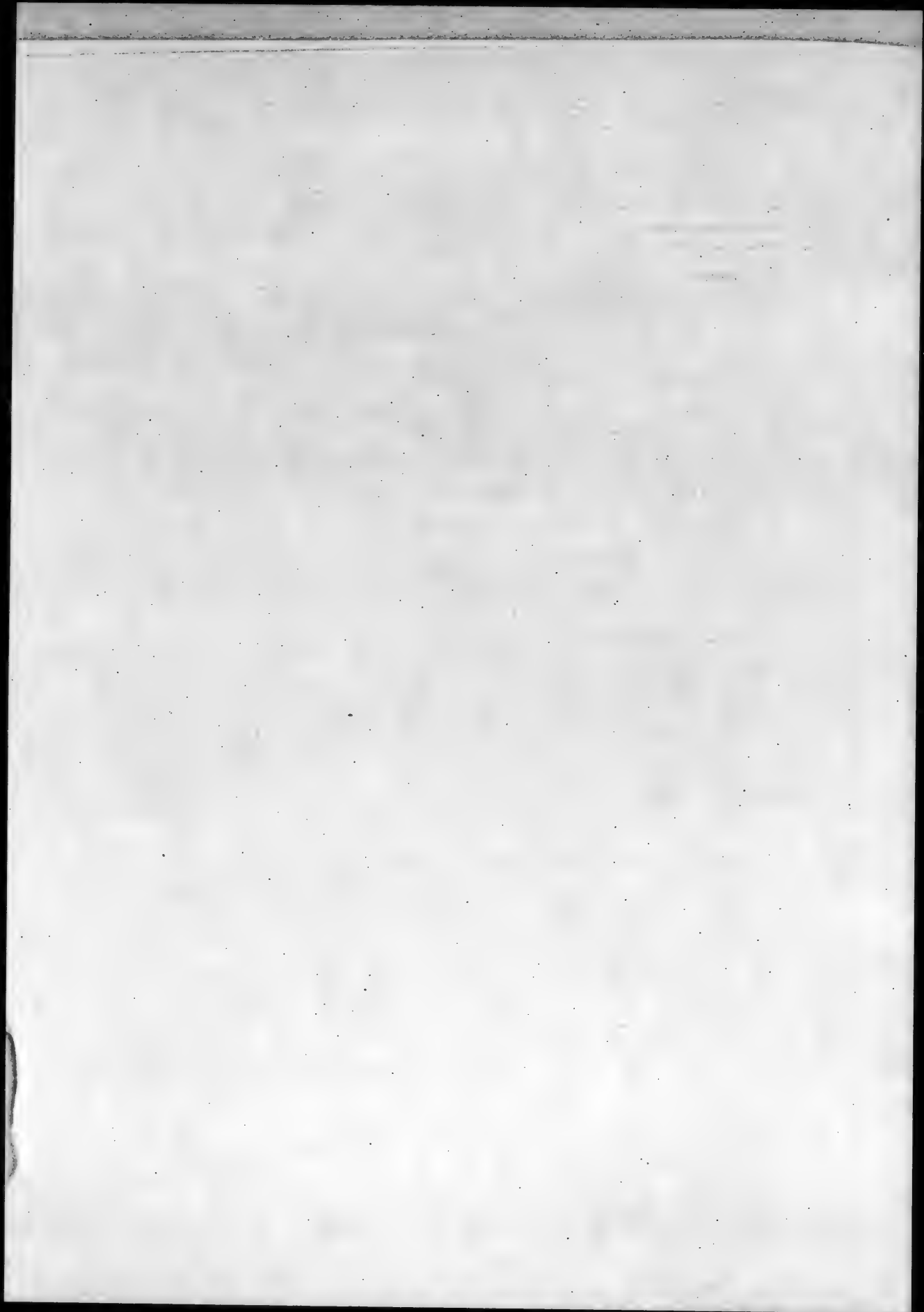
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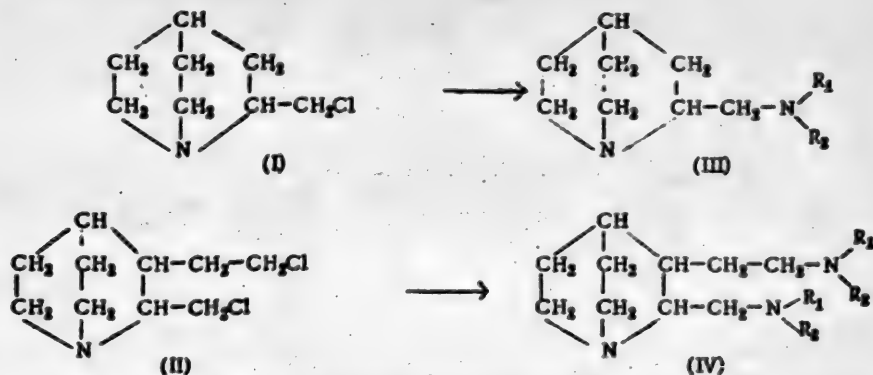


# ALKYLAMINO DERIVATIVES OF QUINUCLIDINE

M. V. Rubtsov, E. S. Nikitskaya, E. E. Mikhlina,

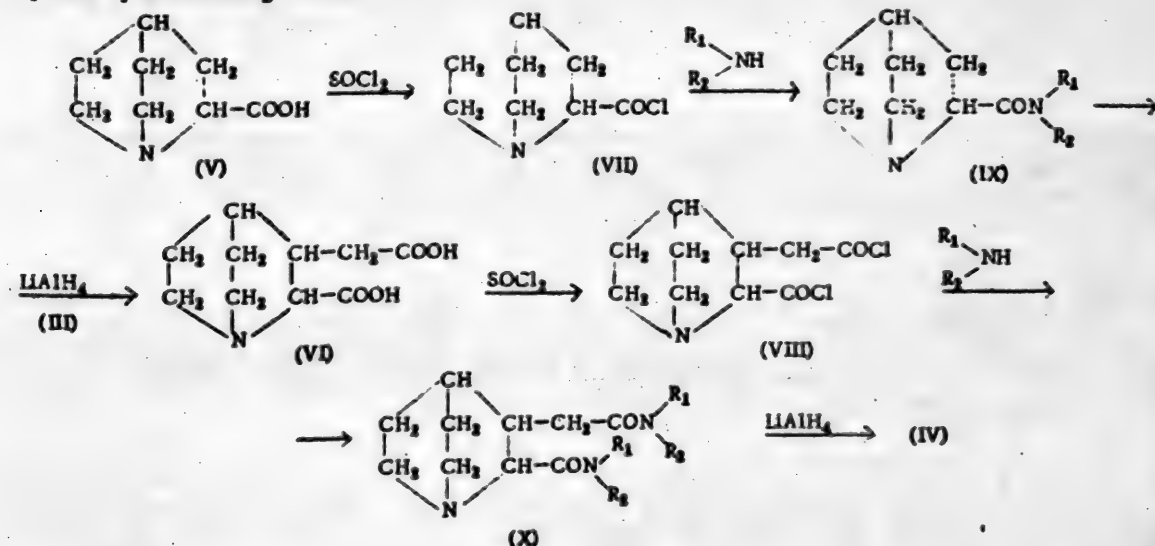
A. D. Yanina, and V. Ya. Furshtatova

Attempts to obtain alkylamino derivatives of quinuclidine from the previously reported chloroderivatives (I and II) [1, 2] were unsuccessful because of the small activity of the chlorine found in the chloromethyl group of the quinuclidine ring.



The synthesis of compounds (III) and (IV) was effected by the reduction of the corresponding amides with lithium aluminum hydride.

The reactions for the preparation of the amides and their reduction into the corresponding amines can be expressed by the following schemes:



2-Quinuclidine carboxylic acid (V) and [2-carboxyquinuclidyl-(3)]-acetic acid (VI) were converted into the acid chlorides (VII and VIII) by means of thionyl chloride. These were treated with ammonia or alkyl (aryl) amines, which resulted in the formation of the corresponding amides (IX and X). Compounds (III) and (IV) were obtained by the reduction of the amides with lithium aluminum hydride.

The yield of the amine depends on the solubility of the starting amide in ether, or benzene in which the reduction reaction was conducted. With sufficiently good solubility of the amide in the above solvents, the amines are obtained with yields of 70-80%. Poor solubility of the amide leads to a sharp decrease of the yield. Thus, 2-quinuclidine carboxamide [3], difficultly soluble in ether and insoluble in benzene, is reduced with a yield of about 40% of the amine, [2-carboxyquinuclidyl-(3)]-acetic diamide, practically insoluble in ether and benzene, does not react with lithium aluminum hydride.

## EXPERIMENTAL

### 2-Quinuclidine Carboxylic Dimethylamide

1.5 g of 2-quinuclidine carboxyl chloride was heated for 8 hours with 15 ml of thionyl chloride at 60-65°. The excess thionyl chloride was removed in vacuum, the remainder was removed by the two-fold addition of 20 ml of absolute benzene followed by its distillation. The 2-quinuclidine carboxyl chloride hydrochloride obtained was added gradually with cooling to 50 ml of 10% solution of dimethylamine in absolute ether. The reaction mixture was then shaken with 10 ml of a 50% solution of potassium carbonate, the ether solution was separated, dried with potassium carbonate, the solvent removed in vacuum, and the residue distilled at 0.34 mm. 0.8 g of a substance with a b.p. of 97-100° was obtained. The substance crystallized upon cooling in the form of white crystals with an m.p. of 48-50°. The yield was 57% of the theoretical. The substance was readily soluble in ether, chloroform, and alcohol, poorly in water.

4.089 mg substance: 9.901 mg CO<sub>2</sub>; 3.586 mg H<sub>2</sub>O. 6.790 mg substance: 7.42 ml 0.01 N H<sub>2</sub>SO<sub>4</sub>.  
Found %: C 66.08; H 9.81; N 15.30. C<sub>14</sub>H<sub>22</sub>ON<sub>2</sub>. Calculated %: C 65.92; H 9.89; N 15.38.

### 2-Quinuclidine Carboxylic Diethylamide

The acid chloride obtained from 1.5 g of 2-quinuclidine carboxylic acid hydrochloride was treated in the manner reported above with a solution of 8.75 g of diethylamine in 15 ml of absolute benzene. 1.65 g of a substance with b.p. 100-102° at 0.35 mm was obtained. Yield, 75% of the theoretical amount. It was a colorless, oil-like liquid readily soluble in organic solvents and in water.

3.763 mg substance: 9.399 mg CO<sub>2</sub>; 3.502 mg H<sub>2</sub>O. 6.770 mg substance: 6.39 ml 0.01 N H<sub>2</sub>SO<sub>4</sub>.  
5.666 mg substance: 5.32 ml 0.01 N H<sub>2</sub>SO<sub>4</sub>. Found %: C 68.16; H 10.41; N 13.21, 13.14.  
C<sub>16</sub>H<sub>24</sub>ON<sub>2</sub>. Calculated %: C 68.55; H 10.47; N 13.33.

### [2-Carboxyquinuclidyl-(3)]-acetic Diamide

[2-Carboxyquinuclidyl-(3)]-acetyl dichloride hydrochloride, obtained from 3 g of the acid hydrochloride in the same manner as for 2-quinuclidine dicarboxylic acid hydrochloride, was suspended in 90 ml of absolute ether and the suspension saturated with ammonia. 40 ml of a 50% potassium carbonate solution was added to it, and it was well stirred. The precipitate, containing the diamide and a small amount of ammonium chloride, was filtered and air dried. The residue was mixed with 50 ml of absolute alcohol, the alcoholic solution filtered from the insoluble ammonium chloride, decolorized with carbon, and evaporated to a volume of 15 ml. Upon cooling, 1.7 g of [2-carboxyquinuclidyl-(3)]-acetic diamide formed. M.p. 198-200°; yield, 66.8% of the theoretical. It was a white crystalline powder, readily soluble in water, soluble in alcohol upon heating, and insoluble in chloroform, acetone, ether, and benzene.

2.418 mg substance: 0.412 ml N<sub>2</sub> (22.5°, 747 mm). Found %: N 19.33. C<sub>16</sub>H<sub>24</sub>O<sub>3</sub>N<sub>2</sub>. Calculated %: N 19.9.

### 2-Carboxyquinuclidyl-(3)]-acetic Di-(dimethylamide)

[2-Carboxyquinuclidyl-(3)]-acetyl dichloride hydrochloride, obtained from 3 g of the acid hydrochloride, was treated with 45 ml of an 18% ether solution of dimethylamine. 2.56 g of a substance with b.p. 165-170° at 0.2 mm was obtained. Yield, 79.7% of the theoretical. The vacuum distilled product crystallized upon cooling; m.p. 117-118°. It was readily soluble in water, alcohol, chloroform, and acetone, difficultly in ether.

4.159 mg substance: 9.610 mg CO<sub>2</sub>; 3.385 mg H<sub>2</sub>O. 5.436 mg substance: 6.23 ml 0.01 N H<sub>2</sub>SO<sub>4</sub>.  
Found %: C 63.05; H 9.11; N 16.05. C<sub>14</sub>H<sub>22</sub>O<sub>3</sub>N<sub>2</sub>. Calculated %: C 62.92; H 9.36; N 15.72.

### [2-Carboxyquinuclidyl-(3)]-Acetic Di-(diethylamide)

[2-Carboxyquinuclidyl-(3)]-acetyl dichloride hydrochloride, obtained from 3 g of the acid hydrochloride, was treated with a solution of 8.8 g of diethylamine in 20 ml of absolute benzene. After the usual processing, 3.2 g



of a substance with b.p. 163-165° at 0.4 mm was obtained. Yield, 32.2% of the theoretical. It was a viscous, yellow liquid which crystallized upon prolonged standing; m.p. 45°. The substance was readily soluble in water and in organic solvents.

4.448 mg substance; 10.921 mg CO<sub>2</sub>; 4.069 mg H<sub>2</sub>O. 3.265 mg substance: 3.10 ml 0.01 N H<sub>2</sub>SO<sub>4</sub>.  
Found %: C 67.00; H 10.23; N 13.27. C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>. Calculated %: C 66.87; H 10.41; N 13.00.

### [2-Carboxyquinuclidyl-(3)]-acetic Dibenzylamide

[2-Carboxyquinuclidyl-(3)]-acetyl dichloride hydrochloride, obtained from 2 g of the acid hydrochloride, was added with stirring and cooling to a solution of 4.28 g of benzylamine in 40 ml of absolute ether. A voluminous precipitate, a mixture of [2-carboxyquinuclidyl-(3)]-acetic dibenzylamide and benzylamine hydrochloride formed. 40 ml of chloroform was added to the mixture to dissolve the dibenzylamide. Benzylamine hydrochloride was filtered and washed on the filter with another 40 ml of chloroform, the chloroform solution was evaporated in vacuum, and the dry residue was recrystallized from 10 ml of alcohol. 2.1 g of white crystals with m.p. 139-141° was obtained. Yield, 67.7% of the theoretical. The substance was readily soluble in chloroform, soluble in alcohol upon heating, poorly soluble in water, and insoluble in ether.

3.589 mg substance: 9.714 mg CO<sub>2</sub>; 2.422 mg H<sub>2</sub>O. 5.534 mg substance: 0.511 ml N<sub>2</sub> (22°, 729 mm).  
Found %: C 73.86; H 7.55; N 10.24. C<sub>24</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub>. Calculated %: C 73.66; H 7.42; N 10.73.

### 2-Aminomethylquinuclidine

Because of the poor solubility of 2-quinuclidine carboxamide in ether [3] the reduction of the latter was conducted in a Tilepape extractor.

1.38 g of 2-quinuclidine carboxamide was placed in the cartridge. 85 ml of absolute ether and 0.85 g of lithium aluminum hydride were charged into the flask. The reaction mass was heated for 20 hours at a slow boil. At the end of the reaction, 1.34 ml of water was added with cooling to the flask. The precipitate of lithium and aluminum hydroxides which formed, was filtered, washed with chloroform, the precipitate transferred to a separatory funnel, 10 ml of a 50% solution of potassium carbonate was added, and it was extracted with chloroform. The chloroform extract was dried with potassium carbonate, the solvent was removed in vacuum, and the residue distilled at 83-85° at 5 mm. 0.5 g of a colorless oily substance was obtained which was readily soluble in organic solvents and in water. Yield, 40% of the theoretical.

4.990 mg substance: 6.95 ml 0.01 N H<sub>2</sub>SO<sub>4</sub>. Found %: N 19.49. C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>. Calculated %: N 20.20.

2-Aminomethylquinuclidine dihydrochloride was a white crystalline powder which was soluble in alcohol and water, and insoluble in ether, with m.p. 277-279° (from alcohol).

5.327 mg substance: 5.04 ml 0.01 N H<sub>2</sub>SO<sub>4</sub>. 6.060 mg substance: 8.281 mg AgCl. Found %: N 13.24; Cl 33.73. C<sub>7</sub>H<sub>12</sub>N<sub>2</sub>Cl<sub>2</sub>. Calculated %: N 13.14; Cl 33.33.

### 2-Dimethylaminomethylquinuclidine

A solution of 2 g of 2-quinuclidine carboxylic dimethylamide in 40 ml of absolute ether was gradually added with stirring to a solution of 1 g of lithium aluminum hydride in 40 ml of absolute ether. At the end of the addition, the reaction mixture was boiled for 20 hours, and then cooled, and 1.6 ml of water was added. The subsequent processing was the same as the above.

1.52 g of a substance with b.p. 89-90° at 7.5 mm was obtained. Yield, 82% of the theoretical. It was a colorless oil-like liquid readily soluble in organic solvents and in water.

2.940 mg substance: 3.43 ml 0.01 N H<sub>2</sub>SO<sub>4</sub>. 3.847 mg substance: 0.563 ml N<sub>2</sub> (25°, 737 mm).  
Found %: N 16.30, 16.21. C<sub>10</sub>H<sub>18</sub>N<sub>2</sub>. Calculated %: N 16.66.

2-Dimethylaminomethylquinuclidine dipicrate was a yellow crystalline substance with m.p. 211.5-213.5° (from alcohol).

4.561 mg substance: 7.129 mg CO<sub>2</sub>; 1.743 mg H<sub>2</sub>O. 4.268 mg substance: 6.651 mg CO<sub>2</sub>; 1.703 mg H<sub>2</sub>O.  
2.190 mg substance: 2.78 ml 0.01 N H<sub>2</sub>SO<sub>4</sub>. Found %: C 42.65, 42.52; H 4.28, 4.46; N 17.77.  
C<sub>22</sub>H<sub>26</sub>O<sub>4</sub>N<sub>2</sub>. Calculated %: C 42.17; H 4.15; N 17.89.

## 2-Diethylaminomethylquinuclidine

3.22 g of 2-quinuclidine carboxylic diethylamide was reduced with 1 g of lithium aluminum hydride in 40 ml of ether. 2.44 g of a substance with b.p. 131-132° was obtained. Yield 81% of the theoretical. It was a syrupy colorless liquid soluble in organic solvents and in water.

3.539 mg substance: 0.443 ml N<sub>2</sub> (22°, 760 mm). Found %: N 13.68. C<sub>14</sub>H<sub>24</sub>N<sub>2</sub>. Calculated %: N 13.77.

2-Diethylaminomethylquinuclidine dipicrate was a yellow crystalline substance with m.p. 196-198° (from 50% alcohol).

4.19 mg substance: 7.128 mg CO<sub>2</sub>; 1.759 mg H<sub>2</sub>O. 4.240 mg substance: 6.842 mg CO<sub>2</sub>; 1.771 mg H<sub>2</sub>O.

4.168 mg substance: 5.17 ml 0.91 N H<sub>2</sub>SO<sub>4</sub>. Found %: C 44.02, 44.04; H 4.45, 4.68; N 17.36.

C<sub>24</sub>H<sub>32</sub>O<sub>14</sub>N<sub>2</sub>. Calculated %: C 44.03; H 4.58; N 17.12.

## 2-Dimethylaminomethyl-3-(β-dimethylaminoethyl)-quinuclidine

2.4 g of [2-carboxyquinuclidyl-(3)]acetic di-(dimethylamide) was reduced with 1.5 g of lithium aluminum hydride in a mixture of 30 ml of ether and 30 ml of benzene. 1.64 g of a substance with b.p. 98° at 0.3 mm was obtained. Yield, 76.3% of the theoretical. It was a colorless, mobile liquid, readily soluble in water and organic solvents.

2.965 mg substance: 0.470 ml N<sub>2</sub> (23.5°, 724 mm). Found %: N 17.39. C<sub>14</sub>H<sub>26</sub>N<sub>2</sub>. Calculated %: N 17.57.

2-Dimethylaminomethyl-3-(β-dimethylaminoethyl)-quinuclidine tripicrate was a yellow crystalline substance with m.p. 196-197° (from acetone).

3.120 mg substance: 4.720 mg CO<sub>2</sub>; 1.134 mg H<sub>2</sub>O. 3.027 mg substance: 3.95 ml 0.01 N H<sub>2</sub>SO<sub>4</sub>.

Found %: C 41.55; H 4.06; N 18.27. C<sub>22</sub>H<sub>32</sub>O<sub>11</sub>N<sub>12</sub>. Calculated %: C 41.47; H 4.10; N 18.12.

## 2-Diethylaminomethyl-3-(β-diethylaminoethyl)-quinuclidine

1.3 g of [2-carboxyquinuclidyl-(3)]acetic di-(diethylamide) was reduced in 30 ml of dry ether. 0.95 g of a substance with b.p. 125-127° at 0.26 mm was obtained. Yield, 82.7% of the theoretical. It was a colorless, lively liquid readily soluble in water and in organic solvents.

4.035 mg substance: 10.867 mg CO<sub>2</sub>; 4.625 mg H<sub>2</sub>O. 4.300 mg substance: 11.538 mg CO<sub>2</sub>; 4.809 mg H<sub>2</sub>O.

2.632 mg substance: 0.343 ml N<sub>2</sub> (20°, 726 mm). 2.713 mg substance: 0.348 ml N<sub>2</sub> (23°, 728 mm).

Found %: C 73.49, 73.23; H 12.82, 12.51; N 14.50, 14.17. C<sub>18</sub>H<sub>27</sub>N<sub>2</sub>. Calculated %: C 73.22; H 12.54; N 14.24.

## 2-Benzylaminomethyl-3-(β-benzylaminoethyl)-quinuclidine

1.16 g of a substance with b.p. 230-232° at 0.3 mm was obtained by the reduction of 1.72 g of [2-carboxyquinuclidyl-(3)]acetic dibenzylamide by the action of 0.8 g of lithium aluminum hydride in 100 ml of absolute benzene. Yield, 72% of the theoretical. It was a viscous, yellow liquid, readily soluble in water and organic solvents.

4.482 mg substance: 12.869 mg CO<sub>2</sub>; 3.605 mg H<sub>2</sub>O. 5.407 mg substance: 15.596 mg CO<sub>2</sub>; 4.260 mg H<sub>2</sub>O. Found %: C 78.35, 78.71; H 9.00, 8.82. C<sub>24</sub>H<sub>30</sub>N<sub>2</sub>. Calculated %: C 78.74; H 9.1.

## SUMMARY

A series of substituted 2-aminomethylquinuclidines and 2-aminomethyl-3-(β-aminoethyl)-quinuclidines was synthesized.

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Received June 3, 1953.

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# INVESTIGATION OF COMPOUNDS CONTAINING A THREE-MEMBERED OXIDE RING

## VL REACTION OF ETHYL $\beta$ -METHYL- $\beta$ -ETHYLGLYCIDATE WITH ANILINE

V. F. Martynov and Ya. A. Kastron

The results of the reaction between ethyl  $\beta$ , $\beta$ -dimethylglycidate and aniline and its homologs were reported in the previous communications. It was shown that in all cases the oxide ring of the above glycidic acids was opened from the side of the  $\beta$ -carbon atom, and a  $\beta$ -arylamino substituted  $\alpha$ -hydroxyisovaleric acid is formed.

The present study is an extension of the above investigation. The reaction between the ethyl glycidate and the aniline was effected, as in the previous cases, by heating a mixture of the two at 170-180°, in a sealed tube.

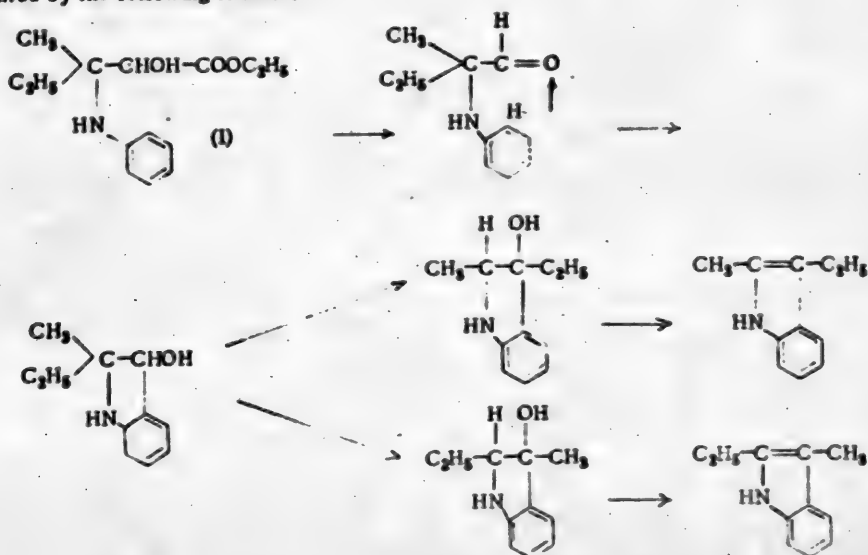
The investigation showed that the oxide of  $\beta$ -methyl- $\beta$ -ethylglycidic acid was considerably more stable than that of  $\beta$ , $\beta$ -dimethylglycidic acid; the addition of aniline proceeded with considerably more difficulty in the first case than in the second.

The heating of ethyl  $\beta$ -methyl- $\beta$ -ethylglycidate with aniline for 6 hours at the above temperature led to only a 20% yield of the addition product, while under analogous conditions, ethyl dimethylglycidate formed an addition product with a 60% yield with aniline.

In order to attain a satisfactory yield of the reaction product, it was found necessary to increase the heating time of the reaction mixture sharply. Thus, a 50% yield could only be obtained by a 50-hour heating. Such a sharp difference in the reactivity of the above glycidic acids is explained, possibly, by the increased steric hindrance upon changing the methyl group to an ethyl group on the  $\beta$ -carbon atom.

The product of the addition of aniline to ethyl  $\beta$ -methyl- $\beta$ -ethylglycidate was a crystalline compound to which, on the basis of the previously conducted investigations, the formula of ethyl  $\alpha$ -hydroxy- $\beta$ -anilinylisocaproate (I) could be assigned with a great degree of certainty.

For a conclusive proof of the certainty of this formula, the compound obtained was heated with strong sulfuric acid. An intense evolution of carbon monoxide occurred at 110-115° which, as is known, is a property of  $\alpha$ -hydroxy acids. The second fragment of the molecule, under such a decomposition, must have been the corresponding amino aldehyde which could not have remained unchanged under the conditions of the given reaction, and which must have been, judging from previous studies, converted into methylethylindole. However, the formation of two isomeric methylethylindoles should have been expected upon the closing of the indole ring in this case. The isomerism can be illustrated by the following scheme:



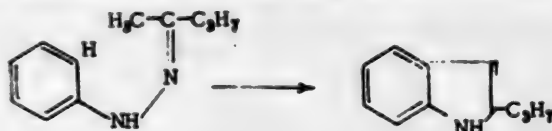
As is apparent from the given scheme, 2-methyl-3-ethylindole, 3-methyl-2-ethylindole, or a mixture of the two isomers could have been obtained as a result of the above transformations. Both isomeric indoles are known from the literature. 3-Methyl-2-ethylindole is a solid with a melting point, according to one literature reference, of 66° [1] and 59°, according to another [2]. 2-Methyl-3-ethylindole, according to one reference, is a liquid with b.p. 291-293° (750 mm) [3, 4], and a crystalline compound with m.p. 44-45°, according to another [5].

A crystalline compound with a strong fecal odor and m.p. of 44.5-45° was obtained. All analyses upheld the formula of methylethylindole for it.

Therefore, this investigation showed, without any doubt, that the opening of the oxide ring by the action of aniline occurs from the side of the  $\beta$ -carbon atom for ethyl- $\beta$ -methyl- $\beta$ -ethylglycidate. The addition product must be assigned the structure ethyl  $\alpha$ -hydroxy- $\beta$ -anilino-isocaproate

In addition it was necessary to prove the structure of the methylethylindole obtained. This problem was complicated by the fact that, as was shown above, there was disagreement on the physical constants of 2-methyl-3-ethylindole, and therefore, there was no rigidly established standard for comparison.

Such a disagreement in the physical properties of 2-methyl-3-ethylindole can be explained by the method of its preparation. All of the authors started with Fischer's method, i.e., the decomposition of the methylpropyl ketone phenylhydrazone, whereby they believed that the reaction proceeds only in one direction, the formation of 2-methyl-3-ethylindole, and completely neglected the second possibility of the formation of 2-propylindole.



even though the reaction undoubtedly occurred.

It is not surprising, therefore, that 2-methyl-3-ethylindole was characterized until recently as a liquid. The small impurity of propylindole sharply lowered the melting point. Only in 1947 was a pure preparation of crystalline structure obtained [5].

In order to prove the structure of the methylethylindole obtained, both of the possible isomers were synthesized; 2-methyl-3-ethyl indole, synthesized by Fischer's method, was a liquid. The mixed melting point of the compound obtained with the crystalline isomer of 3-methyl-2-ethylindole gave a strong depression. This served as an indirect proof that the isomeric 2-methyl-3-ethylindole was obtained.

For final proof, picrates of both isomeric indoles were obtained, and a mixed melting point of the two was initially taken; a large depression occurred. Then mixed melting points of the picrate of the methylethylindole obtained with those of the two isomeric forms of methylethylindole were taken. A depression was absent only upon melting with 2-methyl-3-ethylindole picrate.

Therefore, 2-methyl-3-ethylindole was obtained as a result of the action of sulfuric acid upon ethyl- $\alpha$ -hydroxy- $\beta$ -anilinoisocaproate. Thus, the retro-pinacol rearrangement occurred selectively during the closing of the indole ring, with the ethyl group migrating.

## EXPERIMENTAL

### Preparation of Ethyl- $\alpha$ -Hydroxy- $\beta$ -anilinoisocaproate

A mixture consisting of 31.6 g of ethyl  $\beta$ -methyl- $\beta$ -ethyl glycidate and 55.8 g of aniline was sealed into a glass ampoule, which was then heated for 40 hours (with interruptions) at 170-180°. The contents of the tube turned red, and some pressure was detected upon opening.

A fraction boiling at 150-154° (3 mm) was collected upon vacuum distillation, which was a yellow, viscous liquid which rapidly crystallized. 25 g (50%) was obtained. After 4 recrystallizations from ligroin, the white crystalline compound had an m.p. 59-60°.

0.4686 g substance: 22.6 ml  $N_2$  (19°, 761.5 mm). 0.4435 g substance: 22.9 ml  $N_2$  (20°, 759 mm).  
0.1500 g substance: 15.26 g  $C_6H_6$   $\Delta t$  0.20°. 0.9454 g substance: 13.70 g  $C_6H_6$   $\Delta t$  1.42°. Found %:  
N 5.18, 5.30; M 252.1, 248.8.  $C_{14}H_{17}O_2N$ . Calculated %: N 5.57, M 251.

For the determination of carbon monoxide during the decomposition of ethyl  $\alpha$ -hydroxy- $\beta$ -anilinoisocaproate by the action of concentrated sulfuric acid, an apparatus and procedure was used which was applied for the analysis of tertiary and secondary fatty acids [6].

The heating with sulfuric acid was conducted at 110-115°, i.e., at that temperature at which the decomposition of the secondary, indole, component of the reaction did not occur.

0.3890 g substance: 34.5 ml CO (17°, 756.5 mm). 0.4156 g substance: 38.3 ml CO (17°, 756.5 mm).

Found %: CO 11.09, 11.50.  $C_{14}H_{13}O_3N$ . Calculated %: CO 11.15.

#### Transformation of Ethyl $\alpha$ -Hydroxy- $\beta$ -anilinoisocaproate into 2-Methyl-3-ethylindole

15 g of ethyl  $\alpha$ -hydroxy- $\beta$ -anilinoisocaproate was added to 50 ml of concentrated sulfuric acid; a complete solution occurred with shaking and slight heating. At 95° (thermometer within the mixture), the formation of gas bubbles started to occur (carbon monoxide). At 110-115° there was an intense evolution of carbon monoxide. After the end of the evolution of the gas, the red colored liquid was poured into water with ice, and the acid neutralized with alkali. The substance which formed as an emulsion was extracted with ether. After the usual operations and the removal of the ether, 4.5 ml of a red brown liquid was obtained. The substance distilled in vacuum at 117.5-118° (2 mm), and was a light yellow liquid of average viscosity which rapidly crystallized. 4 g, which was 42%, was obtained. The yield of the product should have been higher since no tarring had occurred, but 2-methyl-3-ethylindole possesses a noticeable solubility, which was mentioned by other authors [3], because of which, evidently, some decrease of the yield occurred. After recrystallization from petroleum ether, the m.p. was 44-44.5°.

Found %: N 9.0; OH 10.9; M 157.7.  $C_{14}H_{13}N$ . Calculated %: N 8.8; OH 10.7; M 159.

The picrate (wine-red thin needles) melted at 150-151° after recrystallization from aqueous alcohol. Literature data: 152-153° [3], 148-149° [5]. A mixed melting point determination with 2-methyl-3-ethylindole which was obtained and authentically synthesized 3-methyl-2-ethylindole gave a m.p. of 26-28° which was a depression of 17° from the lower melting point.

A mixed melting point determination of 2-methyl-3-ethylindole picrate and 3-methyl-2-ethylindole picrate gave a m.p. 128-130°; depression,  $\approx 20^\circ$ . A mixed, melting point determination of 2-methyl-3-ethylindole picrate obtained and that of 3-methyl-2-ethylindole synthesized authentically, gave a m.p. of 131-132°; depression,  $\approx 20^\circ$ . No depression was found in a mixed melting point determination of 2-methyl-3-ethylindole picrate obtained and authentically synthesized 2-methyl-3-ethylindole picrate (m.p. 150°).

#### SUMMARY

1. The reaction between ethyl  $\beta$ -methyl  $\beta$ -ethylglycidate with aniline was studied. It was shown that the opening of the epoxy ring of the above glycidic acid occurs at the side of the  $\beta$ -carbon atom under the action of aniline. Ethyl  $\alpha$ -hydroxy- $\beta$ -anilinoisocaproate, unreported hitherto in the literature, was obtained.
2. The case of selective retropinacolin rearrangement was studied on the example of the preparation of 2-methyl-3-ethylindole
3. A new method for the preparation of 2-methyl-3-ethylindole was developed.

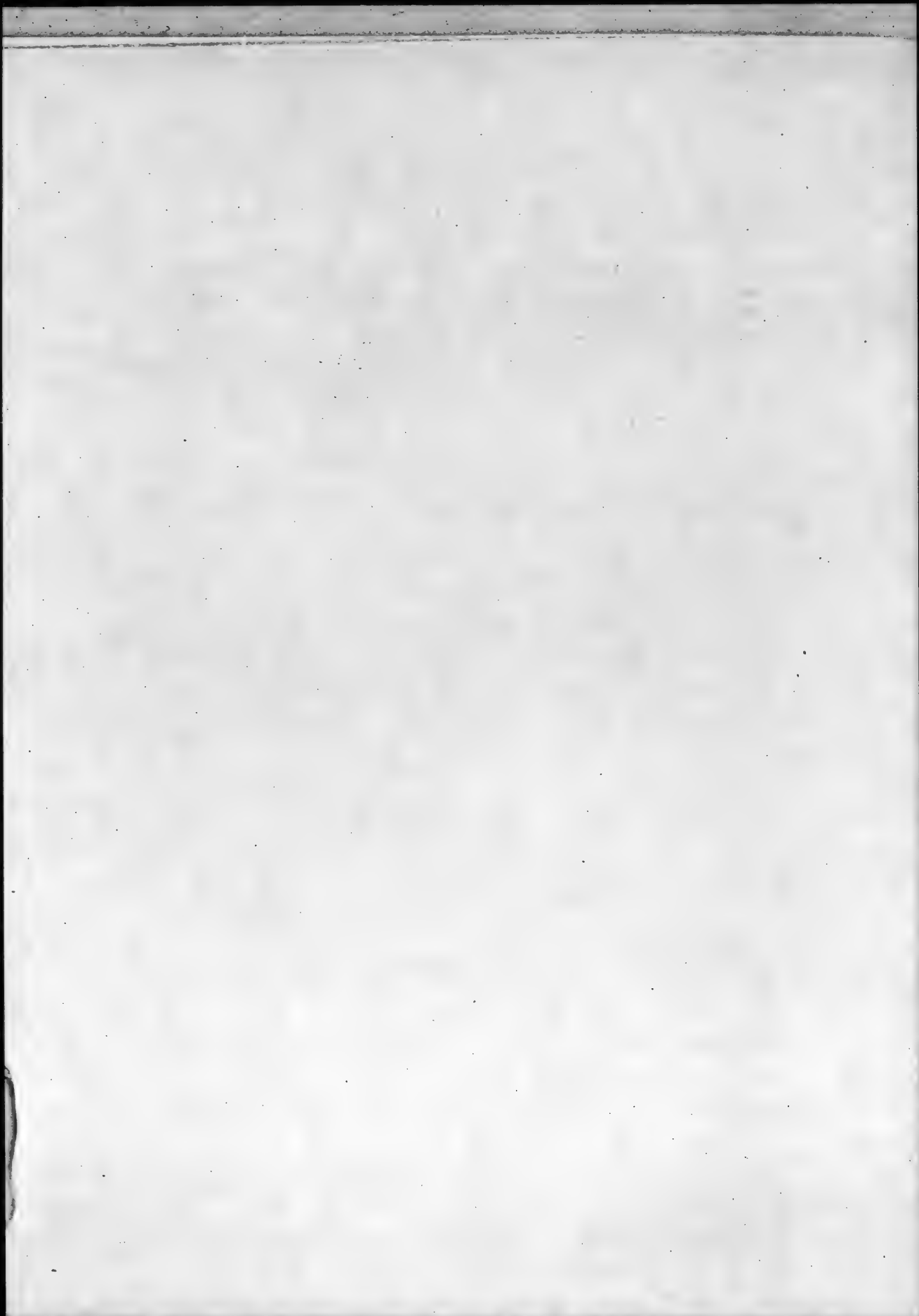
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Received March 20, 1953.

The A. A. Zhdanov Leningrad State University,  
Awarded the Order of Lenin.





# SYNTHETIC INVESTIGATIONS OF INDOLE DERIVATIVES

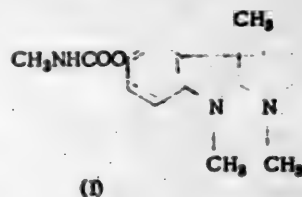
## I. SYNTHESIS OF 1-METHYL-5-HYDROXYINDOLINE AND 1,3-DIMETHYL-5-HYDROXYINDOLINE (DIHYDROPHYSOSTIGMOL) URETHANES

M. N. Kolosov and N. A. Preobrazhensky

The heterocyclic indole (2,3-benzopyrrole) system is of considerable interest as a structural basis of a large number of natural and synthetic substances having important scientific and practical value. The number of indole derivatives also includes such important therapeutic alkaloids as eserine (physostigmine), strychnine, yohimbine, cinchonamine, ergotoxin, ergotamine, and others, growth factors such as indolylacetic acid, as well as natural and synthetic dyes such as indigo.

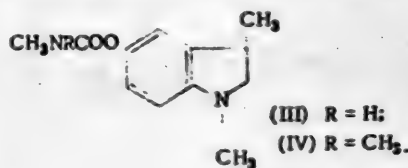
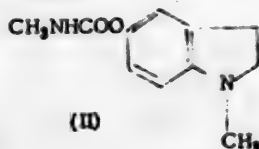
This paper is the first communication of a series on investigations of natural indole compounds and their synthetic analogs.

The alkaloid eserine (physostigmine), the active principle in the fruit of the tropical plant *Physostigma venenosum* (the so-called calabar bean) is the strongest parasympathomimetic substance which blocks choline esterase. Because of its exceptionally strong physiological activity, eserine has a wide application in medicine and veterinary medicine, as well as in biological investigations. It is used mainly as an agent for the lowering of intraocular pressure and as a miotic agent antagonistic to atropine and curarine. The effect of eserine and its analogs (for example proeserine) on the cholinesterase system has found great application recently, especially in the therapy of diseases due to the disruption of the peripheral, as well as the central, nervous system. However, eserine possesses certain drawbacks as a therapeutic agent: it is unstable in aqueous solutions, the organism acquires a rapid tolerance to the preparation which makes an increase of the amount of the substance used necessary. In doses greater than the therapeutic, eserine is very toxic, its largest single dose being only 0.001 g, and the lethal, 0.003 g.



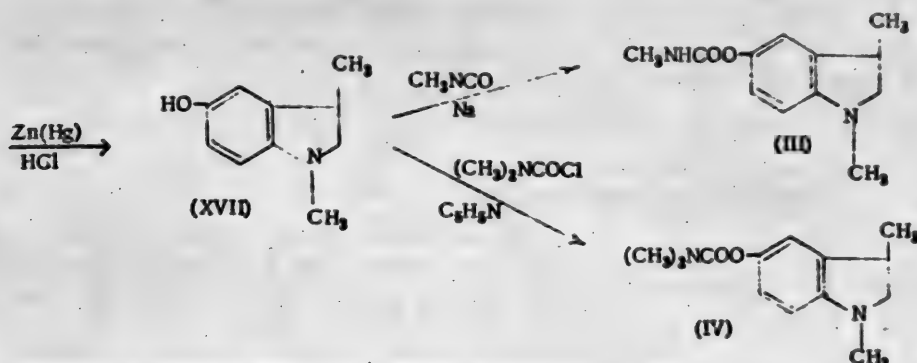
Because of the valuable physiological action of the alkaloid eserine (physostigmine) (I), it is of undoubted interest to prepare simpler substances containing the elements of its structure, as well as to determine the value of these separate elements of this structure in the above substances for the presence of physiological action. The main interest lies in a search for those analogs of eserine which would lack the above drawbacks. After a definite relation between the physiological activity of eserine and the presence of the methylurethane (methylcarbamyl) group in its structure had been established [1] the main direction in the search for synthetic substitutes for eserine was the preparation of various methylurethanes of aromatic aminophenols, and at the present time, the corresponding pyridine derivatives. However, there have been no modifications effected up to now in the structure of eserine itself, and especially in its heterocyclic part, in order to improve the therapeutic properties of this substance.

The synthesis of the simplest indole analog of the alkaloid eserine, 1-methyl-5-hydroxyindoline methylurethane (II), as well as 1,3-dimethyl-5-hydroxyindoline (dihydrophysostigmol) mono and dimethylurethanes (III) and (IV) is reported in the present communication. In contrast to eserine, these substances do not contain a second pyrrolidine ring in their structures.



• See monograph [2], as well as a more recent paper [3].

CCOC1=CC=C(NNC)C=C1 (X) + CC(=O)C(=O)O  $\xrightarrow{H^+}$  CCOC1=CC=C(NN(C)C(=O)O)C=C1 (X)  $\xrightarrow{205^\circ}$  CCOC1=CC=C2C(=C1)C(=CN2C)C(=O)O (XII)  $\xrightarrow{Zn(Hg), HCl}$  CCOC1=CC=C2C(=C1)C(=CN2C)C(=O)O (XIII)  $\xrightarrow{CH_3NCO, Na}$  CCOC1=CC=C2C(=C1)C(=CN2C)C(=O)O (VII)  $\xrightarrow{CH_3NCO, Na}$  CCOC1=CC=C2C(=C1)C(=CN2C)C(=O)O (II)



The following values for the threshold concentrations of substances were obtained by a study of the mitotic action upon rabbits of the analogs of serine reported in the present communication: hydrochloride (II) - 1:2000, methiodide (II) - 1:1000, hydrochloride (III) - 1:100,000, methiodide (III) - less than 1:1000, hydrochloride (IV) - less than 1:1000, and methiodide (IV) - less than 1:1000.

## EXPERIMENTAL

### 1. 1-Methyl-5-methoxyindoline-2-one (VI).

9.4 g (1.00 mole) of technical 1-methyl-5-hydroxyindoline-2-one [4] was dissolved in 80 ml of a 5% solution of potassium hydroxide, filtered from tars, and 7.5 g (1.03 moles) of dimethyl sulfate added with stirring. The mixture was heated on the water bath for 1 hour, keeping an alkaline reaction by further addition of 5% potassium hydroxide solution. The dense oil which separated upon cooling, was extracted with chloroform, the extracts dried with sodium sulfate, and the solvent removed. The residue was distilled and 6.4 g (62.7%) of 1-methyl-5-methoxyindoline-2-one with b.p. 132-136° at 1 mm was obtained. It melted at 96-97° [5] after recrystallization from an ether-methanol mixture.

2.990 mg substance: 7.430 mg  $\text{CO}_2$ ; 1.630 mg  $\text{H}_2\text{O}$ . 3.015 mg substance: 7.490 mg  $\text{CO}_2$ ; 1.675 mg  $\text{H}_2\text{O}$ .

2.565 mg substance: 0.181 ml  $\text{N}_2$  (24°, 731 mm). 3.520 mg substance: 0.245 ml  $\text{N}_2$  (25°, 745 mm).

Found %: C 67.76, 67.70; H 6.10, 6.20; N 7.78, 7.81.  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$ . Calculated %: C 67.76; H 6.26; N 7.91.

### 2. Reduction of 1-Methyl-5-methoxyindoline-2-one

17 g (20.5 g atoms) of sodium was added to a boiling solution of 6.4 g (1.00 mole) of 1-methyl-5-methoxyindoline-2-one in 200 ml of butyl alcohol. The reaction mass was heated to reflux until the start of precipitation of sodium butylate, then 50 ml of butanol was added, and the heating was continued until complete solution of the sodium. Upon cooling, the solution was washed several times with ice water, and the alcohol removed in vacuum. The residue was shaken with 30 ml of water and 20 ml of ether, the crystals which separated (A), were filtered; they weighed 14 g (24.2%). The ether solution was washed with water, dried with sodium sulfate, the ether removed, and residue distilled in vacuum. The fraction 130-160° at 2 mm obtained crystallized. After recrystallization from an ether-methanol mixture, 2.0 g (31.3%) of a substance with m.p. 96-97° was obtained, which did not give depression in a mixed melting point determination with the starting 1-methyl-5-methoxyindoline-2-one.

Substance A was a white crystalline material with an m.p. of 136-136.5° after two recrystallizations from alcohol using carbon.

3.035 mg substance: 8.365 mg  $\text{CO}_2$ ; 1.670 mg  $\text{H}_2\text{O}$ . 3.000 mg substance: 8.250 mg  $\text{CO}_2$ ; 1.665 mg  $\text{H}_2\text{O}$ .

3.195 mg substance: 0.250 ml  $\text{N}_2$  (24°, 746 mm). 3.295 mg substance: 0.250 ml  $\text{N}_2$  (24°, 753 mm).

5.375 mg substance: 63.0 mg camphor:  $\Delta t$  11.13°. 4.035 mg substance: 36.9 mg camphor:  $\Delta t$  14.13°.

Found %: C 75.16, 74.90; H 6.16, 6.21; N 8.83, 8.64; M 307, 310.  $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_2$ . Calculated %: C 74.96; H 6.30; N 8.74; M 320.

The substance was insoluble in water and in aqueous alkali solutions; it dissolved in cold concentrated hydrochloric acid but precipitated upon the addition of water. The compound gave a wine-red color with a pine

• The investigation of the physiological activity of the substances synthesized in the present study was conducted in the S. Ordzhonikidze All-Union Chemico-Pharmaceutical Scientific Research Institute by the students of co-worker I. M. Sharapov under the direction of Prof. M. D. Mashkovsky to whom the authors wish to express their sincerest appreciation.

splinter moistened with hydrochloric acid. The picrate was obtained in alcoholic solution and was recrystallized from alcohol. It was a dark red crystalline substance with m.p. 109°.

### 3. Methyl-p-ethoxyphenylhydrazine (X)

This substance was prepared by means of a method similar to that reported for methylphenylhydrazine [6]. The yield, based upon N-methylphenetidine, was 55%, b.p. 137-140° at 6 mm.

Literature data (7) (b.p. about 140° at 12 mm) evidently result from a mixture of hydrazine (X) and N-methylphenetidine.

### 4. Methyl-p-ethoxyphenylhydrazone of Pyruvic Acid (XI)

17.0 g (1.25 moles) of pyruvic acid was mixed with a solution of 25.6 g (1.00 mole) of methyl-p-ethoxyphenylhydrazine in 75 ml of 50% acetic acid. After standing for 2 hours at room temperature, the reaction mixture was cooled and the crystals which separated were filtered and washed with cold 50% acetic acid and water. After drying in vacuum, 32.8 g (90.3%) of pyruvic acid methyl-p-ethoxyphenylhydrazone with m.p. 68-70° was obtained. The substance melted at 70.5-71.0° after recrystallization from aqueous methyl alcohol, and was a yellowish crystalline substance, very readily soluble in the usual organic solvents.

2.935 mg substance: 6.580 mg CO<sub>2</sub>; 1.760 mg H<sub>2</sub>O. 3.020 mg substance: 6.740 mg CO<sub>2</sub>; 1.200 mg H<sub>2</sub>O.  
2.710 mg substance: 0.294 ml N<sub>2</sub> (25°, 724 mm). 2.825 mg substance: 0.315 ml N<sub>2</sub> (25°, 720 mm).  
Found %: C 61.14, 60.86; H 6.71, 6.67; N 11.82, 12.10. C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>N<sub>2</sub>. Calculated %: C 60.98; H 6.83; N 11.86.

### 5. 1-Methyl-2-carboxy-5-ethoxyindole (XII)

A solution of 32.8 g of pyruvic acid methyl-p-ethoxyphenylhydrazone in 165 ml of glacial acetic acid was heated for 5 minutes at 60-65°, and then 165 ml of water was added, and the reaction mass was heated for 15 minutes more at 60°. The precipitate which formed upon cooling was filtered, the filtrate was diluted with a large amount of water and heated to boiling. The crystals which separated upon cooling were filtered, combined with those previously obtained, and dried in vacuum over potassium hydroxide. 12.6 g (41.4%) of 1-methyl-2-carboxy-5-ethoxyindole with m.p. 185-187° (with decomposition) was obtained. After several recrystallizations from alcohol with carbon, the substance was obtained in the form of colorless needles with m.p. 188° (with decomposition).

3.100 mg substance: 7.460 mg CO<sub>2</sub>; 1.735 mg H<sub>2</sub>O. 3.010 mg substance: 7.225 mg CO<sub>2</sub>; 1.650 mg H<sub>2</sub>O.  
5.445 mg substance: 0.314 ml N<sub>2</sub> (22°, 740 mm). 5.485 mg substance: 0.324 ml N<sub>2</sub> (22°, 740 mm).  
Found %: C 65.63, 65.46; H 6.26, 6.13; N 6.50, 6.66. C<sub>11</sub>H<sub>13</sub>O<sub>3</sub>N. Calculated %: C 65.72; H 5.98; N 6.39.

### 6. 1-Methyl-5-ethoxyindole (XIII)

12.6 g of technical 1-methyl-2-carboxy-5-ethoxyindole was heated to 205-210° on a metal bath until the evolution of carbon dioxide stopped (about 40 minutes), and the 1-methyl-5-ethoxyindole formed vacuum distilled; the distillate crystallized rapidly. 8.7 g of a colorless substance with b.p. 145-148° at 7 mm and m.p. 82-85° was obtained. Yield, 86.5%. After recrystallization from ether, crystals, with m.p. 85-86° [8] were obtained.

3.050 mg substance: 8.450 mg CO<sub>2</sub>; 1.990 mg H<sub>2</sub>O. 3.015 mg substance: 8.370 mg CO<sub>2</sub>; 2.010 mg H<sub>2</sub>O.  
3.975 mg substance: 0.294 ml N<sub>2</sub> (25°, 730 mm). 3.470 mg substance: 0.254 ml N<sub>2</sub> (25°, 730 mm).  
Found %: C 75.55, 75.70; H 7.30, 7.46; N 8.13, 8.05. C<sub>11</sub>H<sub>13</sub>ON. Calculated %: C 75.38; H 7.48; N 8.00.

The picrate crystallized from alcohol in the form of dark red scales with m.p. 96.0-96.5°.

### 7. 1-Methyl-5-hydroxyindoline (VIII)

8.7 g of 1-methyl-5-ethoxyindole was added to 90 g of finely granulated amalgamated zinc in 200 ml of concentrated hydrochloric acid. The reaction mass was refluxed for 9 hours while a stream of hydrogen chloride was passed in, and then for 2 hours more. Upon cooling, the light yellow solution was decanted from the residue, and neutralized with solid sodium bicarbonate. The free base was extracted with ether, the extracts evaporated to approximately 100 ml, washed with water, and dried with sodium sulfate. The residue after the removal of the ether was distilled, and 2.89 g (35.0%) of colorless, 1-methyl-5-hydroxyindoline with b.p. 120-122° at 1 mm and m.p. 79-81° was obtained. After recrystallization from ether, the substance was a white powder with m.p. 83-84°; a mixture with 1-methyl-5-ethoxyindole melted at 63-65°.



3.035 mg substance: 8.050 mg CO<sub>2</sub>; 2.020 mg H<sub>2</sub>O. 3.000 mg substance: 7.980 mg CO<sub>2</sub>; 1.990 mg H<sub>2</sub>O.  
3.660 mg substance: 0.324 ml N<sub>2</sub> (24°, 730 mm). 2.320 mg substance: 0.201 ml N<sub>2</sub> (24°, 730 mm).  
Found %: C 72.33, 72.53; H 7.45, 7.42; N 9.77, 9.56. C<sub>9</sub>H<sub>11</sub>ON. Calculated %: C 72.43; H 7.44; N 9.39.

The picrate was obtained upon mixing hot concentrated solutions of the base and picric acid in alcohol. After recrystallization from ethanol, bright yellow crystals with m.p. 154-155° (with decomposition) were obtained.

The hydrochloride was obtained by the addition of an alcoholic hydrogen chloride solution to a hot alcoholic solution of the base. The crystals which formed upon cooling, were recrystallized from absolute alcohol; m.p. of the hydrochloride, 200-201°.

3.085 mg substance: 6.620 mg CO<sub>2</sub>; 1.755 mg H<sub>2</sub>O. 3.010 mg substance: 6.450 mg CO<sub>2</sub>; 1.725 mg H<sub>2</sub>O.  
3.750 mg substance: 0.260 ml N<sub>2</sub> (25°, 731 mm). 3.920 mg substance: 0.274 ml N<sub>2</sub> (25°, 731 mm).  
Found %: C 58.51, 58.43; H 6.36, 6.41; N 7.64, 7.70. C<sub>9</sub>H<sub>11</sub>ONCl. Calculated %: C 58.23; H 6.52; N 7.54.

#### 8. 1-Methyl-5-hydroxyindoline Methylurethane (II)

1 mg of sodium was added to a solution of 2.89 g (1.00 mole) of 1-methyl-5-hydroxyindoline in 20 ml of absolute benzene, and when the evolution of hydrogen had stopped, a solution of 2.8 g (2.53 moles) of methyl isocyanate (b.p. 39-41°) [11] in 6 ml of absolute benzene was added. The mixture was left to stand for three days in a tightly stoppered bottle at room temperature, filtered from a small amount of a residue, and evaporated in vacuum. After recrystallization of the residue from ether, 3.34 g (83.6%) of colorless 1-methyl-5-hydroxyindoline methylurethane with m.p. 95.5-96.5° was obtained; a mixture with 1-methyl-5-hydroxyindoline melted at 53-57°.

3.135 mg substance: 7.390 mg CO<sub>2</sub>; 1.910 mg H<sub>2</sub>O. 3.010 mg substance: 7.090 mg CO<sub>2</sub>; 1.850 mg H<sub>2</sub>O.  
2.695 mg substance: 0.324 ml N<sub>2</sub> (25°, 745 mm). 2.320 mg substance: 0.274 ml N<sub>2</sub> (23°, 748 mm).  
Found %: C 64.28, 64.24; H 6.82, 6.88; N 13.50, 13.40. C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>N<sub>2</sub>. Calculated %: C 64.04; H 6.86; N 13.58.

The picrate melted at 138-139° after recrystallization from alcohol.

The hydrochloride was obtained from an ethereal solution of the base and an alcohol solution of hydrogen chloride. After recrystallization from butyl alcohol, a white powder with m.p. 152-153° was obtained.

3.025 mg substance: 6.055 mg CO<sub>2</sub>; 1.625 mg H<sub>2</sub>O. 2.995 mg substance: 5.955 mg CO<sub>2</sub>; 1.615 mg H<sub>2</sub>O.  
1.910 mg substance: 0.196 ml N<sub>2</sub> (24°, 746 mm). 2.285 mg substance: 0.235 ml N<sub>2</sub> (24°, 746 mm).  
Found %: C 54.58, 54.22; H 6.01, 6.03; N 11.58, 11.61. C<sub>11</sub>H<sub>13</sub>O<sub>3</sub>N<sub>2</sub>Cl. Calculated %: C 54.41; H 6.23; N 11.54.

The methiodide was obtained in ethereal solution and recrystallized from absolute butanol; colorless crystals with m.p. 205-206° were obtained.

#### 9. 1,3-Dimethyl-5-methoxyindoline-2-one (XV).

It was obtained from technical 1,3-dimethyl-5-hydroxyindole [9] with a yield of 65% by means of a method analogous to that reported above for the synthesis of 1-methyl-5-methoxyindoline-2-one (VI). After recrystallization from ether, it had a m.p. of 86° and a b.p. of 180-182° at 15 mm.

2.985 mg substance: 7.585 mg CO<sub>2</sub>; 1.845 mg H<sub>2</sub>O. 3.650 mg substance: 0.245 ml N<sub>2</sub> (20°, 744 mm).  
Found %: C 69.29; H 6.91; N 7.65. C<sub>11</sub>H<sub>13</sub>O<sub>2</sub>N. Calculated %: C 69.08; H 6.85; N 7.33.

#### 10. 1,3-Dimethyl-5-methoxyindole (XVI) (Physostigmol Methyl Ether)

15 g (1 mole) of 1,3-dimethyl-5-methoxyindoline-2-one was reduced with 50 g (27.6 g atoms) of sodium in 500 ml of absolute butyl alcohol in the same manner as reported for 1-methyl-5-methoxyindoline-2-one. The residue, after the removal of the alcohol, was dissolved in 50 ml of chloroform, the solution washed with water, the solvent removed, and the residue distilled. 10.9 g of a substance with b.p. 159-162° at 14 mm was obtained. Yield, 9.3%. After recrystallization from ether, the m.p. was 60-61° [10].

The picrate was prepared in alcoholic solution and recrystallized from alcohol. It was a dark red crystalline substance with m.p. 116-117°.

### 11. 1,3-Dimethyl-5-hydroxyindoline (XVII) (Dihydrophysostigmol)

10.9 g of physostigmol methyl ether, 100 g of amalgamated zinc, and 250 ml of concentrated hydrochloric acid were heated under the conditions reported for the preparation of 1-methyl-5-hydroxyindoline. The residue after evaporation of the ether extract crystallized. It was washed from an oil-like impurity with cold chloroform, and 5.18 g (51.0%) of colorless dihydrophysostigmol with m.p. 92-94° was obtained. After recrystallization from ether, it had an m.p. 99°.

3.015 mg substance: 8.100 mg CO<sub>2</sub>; 2.180 mg H<sub>2</sub>O. 4.130 mg substance: 0.324 ml N<sub>2</sub> (21°, 735 mm).  
Found %: C 73.26; H 8.09; N 8.80. C<sub>11</sub>H<sub>13</sub>ON. Calculated %: C 73.62; H 8.04; N 8.59.

The picrate was obtained in the usual manner and recrystallized from alcohol; it had a m.p. of 165-166°.

The hydrochloride was prepared in ether solution. It crystallized from ethanol in the form of colorless crystals with a m.p. of 169-170°.

2.915 mg substance: 6.455 mg CO<sub>2</sub>; 1.870 mg H<sub>2</sub>O. 3.160 mg substance: 7.020 mg CO<sub>2</sub>; 2.050 mg H<sub>2</sub>O.  
4.885 mg substance: 0.324 ml N<sub>2</sub> (21°, 724 mm). 4.090 mg substance: 0.234 ml N<sub>2</sub> (25°, 728 mm).  
Found %: C 60.39, 60.58; H 7.18, 7.26; N 7.33, 7.08. C<sub>11</sub>H<sub>13</sub>ONCl. Calculated %: C 60.32; H 7.08; N 7.03.

### 12. 1,3-Dimethyl-5-hydroxyindoline Methylurethane (III) (Dihydrophysostigmol Methylurethane).

1 mg of sodium was added to a solution of 2.0 g (1.00 mole) dihydrophysostigmol in 20 ml of absolute benzene, and after the evolution of hydrogen stopped, 1.7 g (2.43 moles) of methyl isocyanate [11] in 10 ml of benzene. After standing for 24 hours at room temperature, the solution was filtered and evaporated in vacuum. The residue crystallized slowly. After recrystallization from 60% alcohol, 2.26 g (83.7%) of colorless, dihydrophysostigmol methylurethane with m.p. 75-76° was obtained. A mixture with dihydrophysostigmol melted at 48-52°.

2.970 mg substance: 7.130 mg CO<sub>2</sub>; 1.910 mg H<sub>2</sub>O. 3.040 mg substance: 0.358 ml N<sub>2</sub> (25°, 734 mm).  
Found %: C 65.46; H 7.20; N 13.04. C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>. Calculated %: C 65.45; H 7.33; N 12.73.

The picrate was obtained in alcoholic solution and recrystallized from 80% alcohol. It had a m.p. of 127°; a mixture with picric acid melted at 92-94°.

The methiodide was obtained from a methanolic solution with excess of methyl iodide. After recrystallization from alcohol colorless crystals with m.p. 178.0-178.5° (with decomposition) were obtained.

The hydrochloride was obtained from an ethereal solution of the base and an alcoholic hydrogen chloride solution; it crystallized from alcohol in the form of colorless prisms with m.p. 168-168.5° (with decomposition).

2.955 mg substance: 6.090 mg CO<sub>2</sub>; 1.700 mg H<sub>2</sub>O. 3.650 mg substance: 0.362 ml N<sub>2</sub> (22°, 724 mm).  
Found %: C 55.86; H 6.44; N 10.93. C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>Cl. Calculated %: C 56.12; H 6.68; N 10.91.

### 13. 1,3-Dimethyl-5-hydroxyindoline Dimethylurethane (IV) (Dihydrophysostigmol Dimethylurethane).

2.0 g (1.00 mole) dihydrophysostigmol, 4.0 g (3.03 moles) of dimethylcarbamyl chloride (b.p. 165.5-166.5°), and 10 ml of dry pyridine was heated for 3 hours on a metal bath at 140-145°. Upon cooling the reaction mass was evaporated in vacuum, 10 ml of water was added, and again evaporated. This operation was repeated 3-4 times more, and then 40 ml of ether and 20 ml of a 10% potassium hydroxide solution were added. The ether solution was washed with water, dried, and the ether removed. 1.5 ml of 20% hydrochloric acid was added and the mixture left in vacuum over potassium hydroxide until complete solidification. After recrystallization from absolute alcohol, 2.35 g (70.8%) of colorless dihydrophysostigmol dimethylurethane hydrochloride with m.p. 188.5-189.0° was obtained.

3.140 mg substance: 6.685 mg CO<sub>2</sub>; 1.960 mg H<sub>2</sub>O. 3.360 mg substance: 0.318 ml N<sub>2</sub> (21°, 724 mm). 3.130 mg substance: 0.294 ml N<sub>2</sub> (23°, 732 mm). Found %: C 58.06; H 6.98; N 10.46, 10.27. C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub>Cl. Calculated %: C 57.65; H 7.08; N 10.35.

The base, isolated from the hydrochloride by treatment with cold, saturated sodium bicarbonate solution, was a thick, colorless oil which was readily soluble in the usual organic solvents

The picrate was prepared in alcoholic solution and recrystallized from alcohol; yellow needles with a m.p. of 123.5-124.0 were obtained (a mixture with picric acid melted at 78-80°).

The methiodide was obtained by treating an acetone solution of the base with methyl iodide. It crystallized from alcohol in the form of shiny needles with an m.p. of 206-207°.

3.010 mg substance: 4.960 mg CO<sub>2</sub>; 1.550 mg H<sub>2</sub>O. 3.035 mg substance: 4.990 mg CO<sub>2</sub>; 1.435 mg H<sub>2</sub>O.  
5.540 mg substance: 0.377 ml N<sub>2</sub> (21°, 724 mm). 4.670 mg substance: 0.324 mg N<sub>2</sub> (25°, 728 mm).  
Found %: C 44.93, 44.83; H 5.76, 5.29; N 7.52, 7.61. C<sub>14</sub>H<sub>17</sub>O<sub>2</sub>N<sub>2</sub>I. Calculated %: C 44.67; H 5.63; N 7.45.

#### SUMMARY

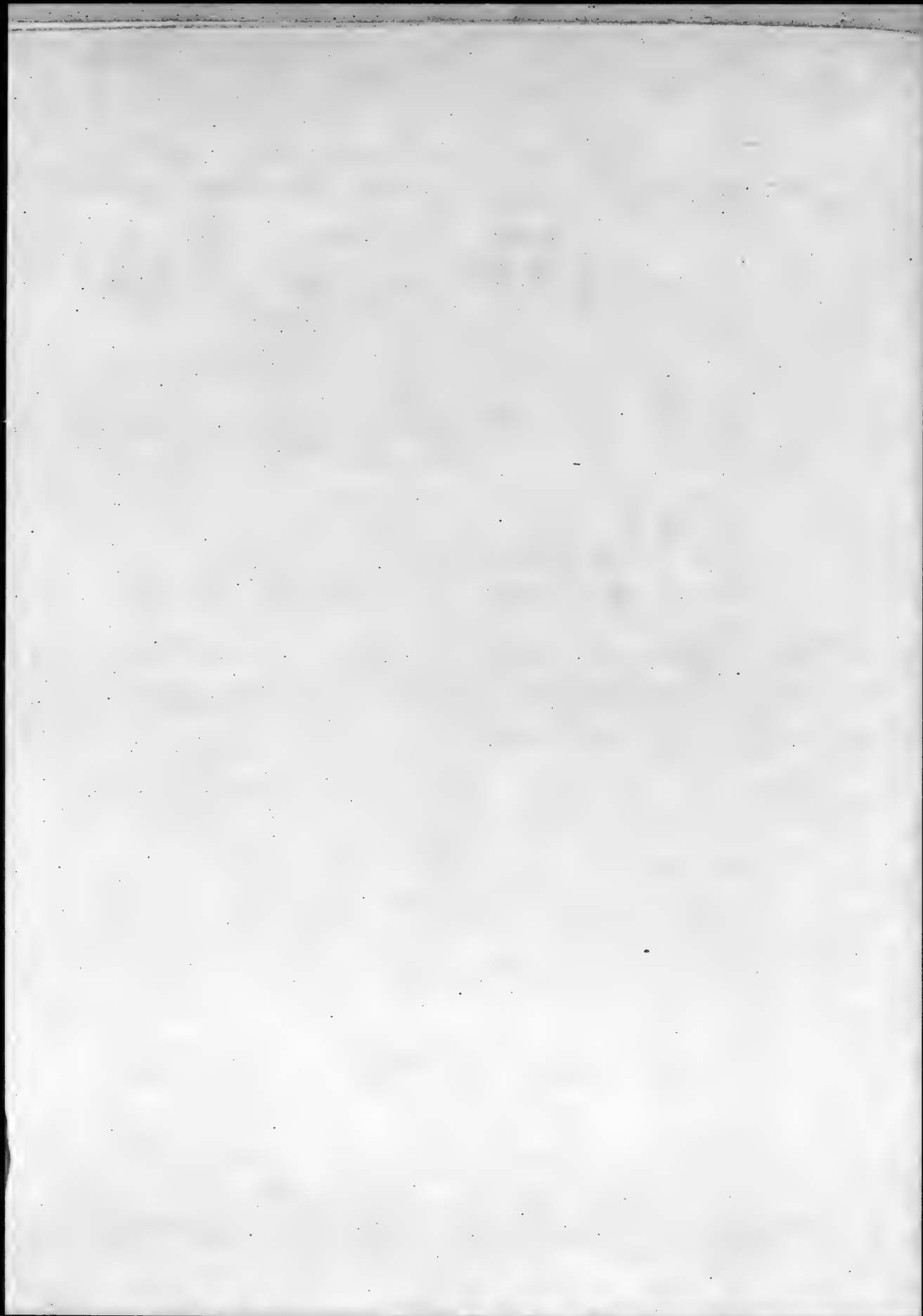
The synthesis of the following analogs of the alkaloid eserine was effected: 1-methyl-5-hydroxyindoline methylethane, and 1,3-dimethyl-5-hydroxyindoline (dihydrophysostigmine) methyl- and dimethylethanes.

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Received May 15, 1953

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Fine Chemical Technology



# REACTION OF HYDROGEN SULFIDE WITH ACETYLENIC AND VINYLACETYLENIC OXIDES

## II. SYNTHESIS OF PHENYLTHIOPHENES

F. Ya. Pervov and N. I. Kudryashova

Recently, it was shown [1] that acetylenic oxides of the type  $\text{R}-\text{C}\equiv\text{C}-\overset{\text{O}}{\underset{\text{R}'}{\text{CH}}}-\text{R}''$  were converted into the corresponding homologs of thiophene by reaction with hydrogen sulfide in the presence of  $\text{Ba}(\text{OH})_2$ . In order to extend the study of this reaction, it was considered desirable to determine whether or not oxides containing a phenyl-group as a substituent for an acetylenic hydrogen would cyclize under these conditions. The following oxides were used for this study (see Table).

The synthesis of these oxides was effected from the chloroalcohols which were obtained by Iotich's method. The oxides are mobile, colorless liquids with a faint odor, which yellow upon storage in the air. They are not very stable thermally; upon heating at ordinary pressure, they rapidly polymerize, forming solid tar-like products which are insoluble in water, ether, and acetone. Upon vacuum distillation (2-10 mm), it is necessary to take small portions (20-25 g). Upon using larger amounts, not more than 60% can be distilled; the rest polymerizes. The process

Oxide No.	Formula	Boiling point (in °)	$n_D^{20}$	$d_4^{20}$	MRD	
					found	calculated
(I)	$\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\underset{\text{O}}{\text{C}(\text{CH}_3)-\text{CH}_2}$ [2]	108-109 at 8 mm	1.5552	1.0278	49.21	4703
(II)	$\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\underset{\text{O}}{\text{C}(\text{C}_2\text{H}_5)-\text{CH}_2}$	111-112 at 4 mm	1.5520	1.0112	54.33	5210
(III)	$\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\underset{\text{O}}{\text{C}(\text{CH}_3)-\text{CH}-\text{CH}_3}$ [3]	121-122 at 8 mm	$n_D^{17}$ 1.5435	$d_4^{17}$ 1.0220	53.2	51.2

of polymerization, evidently, is accelerated by the polymerization products which are obtained during the process of the reaction, since only a small amount of tarring occurs upon redistillation.

A colorless liquid with a faint odor and with a b.p. of 123-124° at 5 mm;  $n_D^{20}$  1.6299,  $d_4^{20}$  1.1102; m.p. 16.5-17° corresponding to  $\alpha$ -phenyl- $\beta'$ -methylthiophene [4], was obtained by the reaction between hydrogen sulfide and 2-methyl-4-phenylepoxy-1,2-butyne-3 (I). A mixed melting point gave no depression.

The substance synthesized dissolves in strong sulfuric acid, gives a violet color with isatin sulfate, and forms a white precipitate with a m.p. of 177-179° with mercuric acetate.

$\alpha$ -Phenyl- $\beta'$ -ethylthiophene was obtained by the reaction of 2-ethyl-4-phenylepoxy-1,2-butyne-3 (II) with hydrogen sulfide. The product has a b.p. of 125-126° at 3 mm,  $n_D^{20}$  1.6115,  $d_4^{20}$  1.0779. It dissolves in strong, sulfuric acid, gives a violet color with isatin sulfate, and forms a precipitate with an m.p. of 194-196° with mercuric acetate.

$\alpha$ -Phenyl- $\alpha',\beta'$ -dimethylthiophene was formed under the same conditions by the reaction of hydrogen sulfide with 3-methyl-5-phenylepoxy-2,3-pentyne-4 (III). The substance synthesized was a yellowish liquid with a b.p. of 139-140° at 5 mm which crystallized in the receiver; m.p. 30-31°. It gives a grape color with isatin in strong sulfuric acid. It forms a white precipitate with mercuric acetate, which decomposes at 240°.

The formation of phenylalkylthiophenes, therefore, has also been effected according to a previously suggested scheme [1].

## EXPERIMENTAL

### 1. Preparation of 2-Ethyl-1-chloro-4-phenylbutyne-3-ol-2

80 g of 1-chlorobutanone-2 was added to  $\frac{1}{4}$  of a mole of phenylacetylenyl magnesium bromide in 400 ml



of absolute ether. The reaction mixture was left standing overnight and then decomposed with 30% acetic acid. The ether solution was dried with  $MgSO_4$ , the ether was removed and the remaining product vacuum distilled. Two fractions were isolated: 1 - unreacted phenylacetylene, 14 g quantity, and 2 - a chloroalcohol with a b.p. of 140-141° at 5 mm, 68 g;  $n_D^{20}$  1.5578,  $d_4^{20}$  1.1067;  $MR_D$  60.77.  $C_{12}H_{12}OClF_3$ . Calculated:  $MR_D$  58.41.

0.1298, 0.1524 g substance: 16.0, 17.6 ml  $CH_4$  (15.5°, 764.3 mm). 0.4168, 0.2005 g substance: 0.2835, 0.1358 g  $AgCl$ . Found %: Act. H 0.499, 0.499; Cl 16.82, 16.75. Calculated %: Act. H 0.483; Cl 16.99.

## 2. Preparation of Oxide (II)

A colorless, mobile liquid with a faint odor was obtained by the treatment of the chloroalcohol with powdered KOH in ether solution.

0.1132, 0.1054 g substance: 0.3407, 0.3222 g  $CO_2$ ; 0.0729, 0.0672 g  $H_2O$ . Found %: C 83.58, 83.42; H 7.21, 7.13.  $C_{12}H_{12}O$ . Calculated %: C 83.68; H 7.02.

## 3. Preparation of $\alpha$ -Phenyl- $\beta'$ -methylthiophene

100 ml of water, 15 g of  $Ba(OH)_2$  and 15 g of oxide (I) were placed into a round-bottomed flask with a mechanical stirrer. Hydrogen sulfide was passed into the reaction mixture for 2.5 hours at 70-80° (until the disappearance of the upper layer of the oxide). Then the calculated amount of acetic acid was added. The solution was extracted with ether, the ether layer separated, dried with  $CaCl_2$ , then with metallic sodium, and vacuum distilled. 9 g of  $\alpha$ -phenyl- $\beta'$ -methylthiophene (54.5%) was obtained.

Found:  $MR_D$  55.84.  $C_{11}H_{10}SF_3$ . Calculated:  $MR_D$  54.05.

0.3930, 0.3131 g substance: 0.6216, 0.4133 g  $BaSO_4$ . Found %: S 18.23, 18.13.  $C_{11}H_{10}S$ . Calculated %: S 18.40.

## 4. Preparation of $\alpha$ -Phenyl- $\beta'$ -ethylthiophene

150 ml of water, 20 g of  $Ba(OH)_2$  and 20 g of oxide (II) were used. The hydrogen sulfide was passed in for 4 hours at 60°. 14.5 g of a substance (66.3%) was isolated which was also redistilled over metallic sodium.

Found:  $MR_D$  60.80.  $C_{12}H_{12}SF_3$ . Calculated:  $MR_D$  58.80.

0.2918, 0.2792 g substance: 0.3037, 0.3511 g  $BaSO_4$ . Found %: S 17.12, 16.88.  $C_{12}H_{12}S$ . Calculated %: S 17.03.

## 5. Preparation of $\alpha$ -Phenyl- $\alpha',\beta'$ -dimethylthiophene

150 ml of water, 20 g of  $Ba(OH)_2$  and 25 g of oxide (III) were used. 17 g of phenyldimethylthiophene (62.9%) was isolated after distillation of metallic sodium in vacuum.

0.2342, 0.1989 g substance: 0.2085, 2440 g  $BaSO_4$ . Found %: S 16.92, 16.85.  $C_{12}H_{12}S$ . Calculated %: S 17.03.

## SUMMARY

1.  $\alpha$ -Phenyl- $\beta'$ -methylthiophene,  $\alpha$ -phenyl- $\beta'$ -ethylthiophene, and  $\alpha$ -phenyl- $\alpha',\beta'$ -dimethylthiophene, previously unreported in the literature, were prepared by the reaction of hydrogen sulfide with the following oxides, respectively: 2-methyl-4-phenylepoxy-1,2-butyne-3, 2-ethyl-4-phenylepoxy-1,2-butyne-3, and 3-methyl-5-phenylepoxy-2,3-pentyne-4.

2. The formation of alkyl-, vinyl-, and phenylthiophenes from acetylenic and vinylacetylenic oxides of

the type  $R-C \equiv \overset{\text{O}}{\underset{\text{R}}{\text{C}}} - CH-R'$  by the action of hydrogen sulfide in the presence of  $Ba(OH)_2$  appears to be a general reaction.

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Received April 24, 1953.

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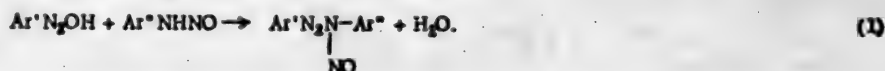
# STRUCTURE AND TRANSFORMATIONS OF N-NITROTRIAZINES

## I. DIARYL-N-NITROTRIAZINES

N. M. Baranchik, I. V. Grachev, and D. Z. Zavel'sky

Among the various forms of diazo compounds, a neutral compound has been known for a long time [1] and has been erroneously regarded as an aryl nitrosoamine [2].

One of the authors [3] investigated this neutral compound by potentiometric titration and by other methods, and showed that it was N-nitrosotriazine (or diazonitrosoamine). N-Nitrosotriazine is readily formed by mixing equimolecular solutions of a diazocompound and a nitrosoaminic acid.



It is also formed by a spontaneous tautomeric transformation of diazodiazate or a nitrosoaminic acid. N-Nitrosotriazine is very unstable: it dissociates into the starting components readily in aqueous solution, and forms an azo compound by action of its active diazo form on the azo component; upon standing, it eliminates the nitroso group to form nitrous acid and diazoamino compounds, and is converted into other forms of diazo compounds by changes in the pH of the medium.

One of the authors [4] first obtained a compound of a new class, N-sulfatotriazine, by the condensation of an active diazo compound with sulfaminic acid and substituted sulfaminic acids:



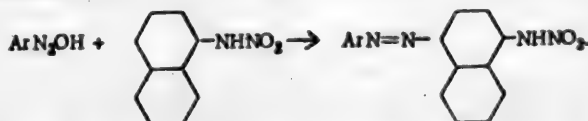
It was found that triazine-N-sulfonic acids were unstable, and in a manner similar to N-nitrosotriazines, could decompose into the starting components or eliminate a sulfo group, the ease of either transformation depending upon the nature of the triazine radicals.

N-Nitrotriazine has not been known up to now. It could be supposed that N-nitrotriazine could be obtained by the condensation of active diazo compounds with nitroaminic acid in analogy to N-nitrosotriazines and N-sulfatotriazines:



There are a large number of papers [5] on nitramines because of their resemblance to diazo compounds and application in several parts of industry. As is shown by G. S. Salyamon, I. V. Grachev, and B. A. Porai-Koshits [6], aryl nitramines have the structure  $\text{ArNHNO}_2$  and are true acids (arylnitraminic acids) which are close in strength to the carboxylic acids and are capable of giving salts of the structure  $\text{ArNMeNO}_2$ . By the action of acids, aryl nitraminic acids are transformed into the corresponding nitroanilines by the transposition of a nitro group into the ring, and into the basic oxodiazohydrates  $\text{ArN}=\text{NOOH}$ .

However, in spite of the similarity of the aryl nitraminic acids to diazo compounds, their reactions have not been studied sufficiently. It is only known that in certain cases this reaction leads to azo coupling in the para position to the nitramino groups [7]:



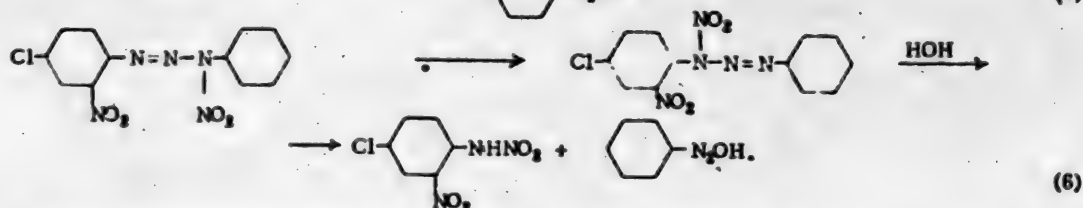
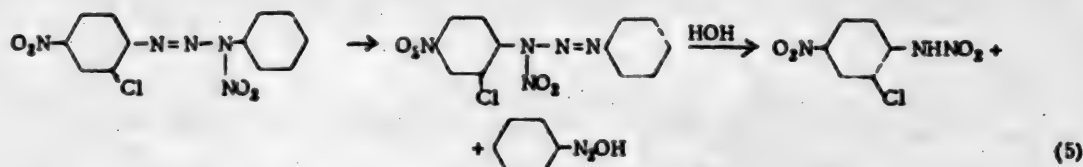
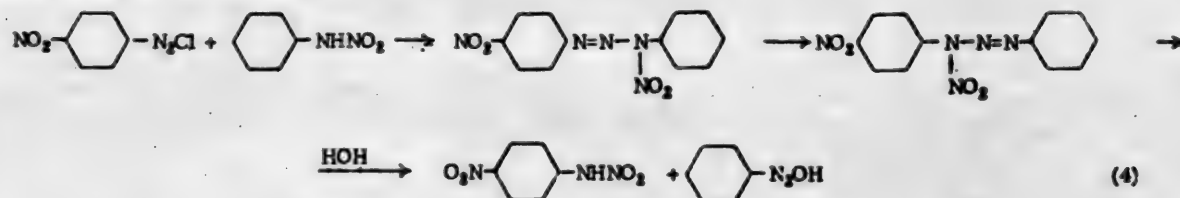
There are no other reactions between diazo compounds and aryl nitraminic acids reported in the literature.

The aim of the present investigation was the preparation of diaryl-N-nitrotriazines by the reaction of active diazo compounds with arylnitraminic acids. The simplest of the nitramine class, phenylnitraminic acid, and the following diazo compounds were chosen for the reaction: p-nitrophenyl-, p-nitro-o-chlorophenyl-, and p-chloro-o-nitrophenyldiazonium. These diazo compounds were chosen because the presence of an electron-attracting group in their phenyl ring insures their diazo coupling activity with such weakly basic amines as phenylnitramines.

The reaction between phenylnitraminic acid and the diazo-compounds, used in equimolecular amounts, was conducted in a weakly-acidic medium (pH 5-6). The isolated condensation product could not be crystallized and analyzed, because of its poor solubility in most solvents and its instability.

New nitraminic acids were isolated from the residue and from the solution, which contained aryl nuclei corresponding to the diazo compound participating in the reaction. In addition, the same new diazo compound was isolated in all cases, which had an aryl radical corresponding to the nitraminic acid participating in the reaction, namely, phenyldiazonium. p-Nitrophenyl-, p-nitro-o-chlorophenyl-, p-chloro-o-nitrophenylnitraminic acids isolated from the reaction mixtures were obtained in the form of crystalline products which were readily identified. Phenyldiazonium was determined by azo coupling in the form of phenyl azo- $\beta$ -naphthol, as well as transformation into phenol, and then, into tribromophenol.

The appearance of the compounds isolated in the reaction products indicated the formation of diaryl-N-nitrotriazine which readily hydrolyzes with the formation of the new nitraminic acid and diazobenzene according to the following reactions:



The authors were first to observe the "transition" of the N-nitro group from the nitrogen to another nitrogen of the triazine which is combined with the nucleus having the electron-attracting substituents, as shown in equations (4), (5), and (6).

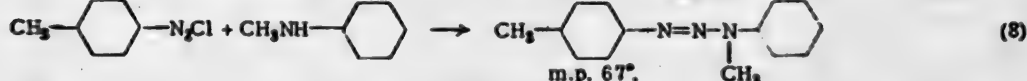
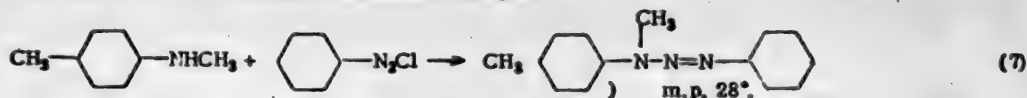
The asymmetric disubstituted triazine is subjected to tautomeric transformations [8] which are due to the movement of the imide hydrogen from one nitrogen of the triazine chain to the other which is combined with the nucleus having the electron attracting substituent:



In spite of the large number of investigations in this field, there is not a single idea relative to the mechanism of the tautomeric transformation of diazoamino compounds up to now. It seems apparent that the position of the imide hydrogen depends on the nature of the radicals, as well as on the pH of the medium in which the triazine is found [9].

A study of the metallic salts of the triazines [10] showed that these salts can be represented as internal complexes in which the triazine system is the chelating part of the molecule. On the basis of the study of the molecular weight of the triazines [11], it was shown that the triazine molecules are associated in solution, and possibly, in solid state. Two forms of association are suggested, linear and cyclic.

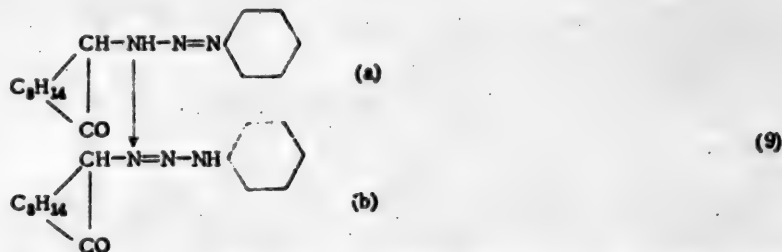
If the imide hydrogen in the diazoamino compound is substituted by an alkyl radical, it loses its ability for tautomeric transformation. Thus, a compound with a single composition with m.p. 28° was obtained from N-methyl-toluidine and diazobenzene [12], another with m.p. 67° from N-methylaniline and diazotoluene. Both of these isomeric compounds showed no tendency to tautomeric changes:



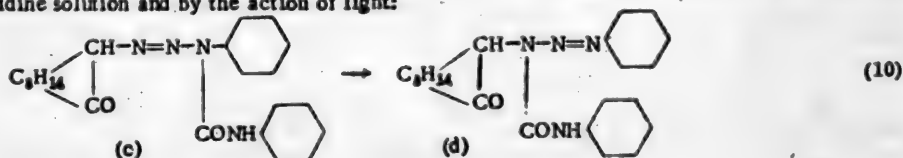
Analogous isomeric compounds with a fixed ethyl group which are incapable of tautomeric transformation [13] can be cited as another example: one compound obtained by the coupling of m-nitrobenzene with ethyl-p-nitroaniline; another, by the coupling of p-nitrodiazobenzene with m-nitroethylaniline. However, if the diazoamino compounds themselves are alkylated, then a mixture of both compounds is obtained.

It must be mentioned that the methyl and sulfo groups in arylmethylsulfotriazines occupy strictly fixed definite positions, and the compounds do not possess tautomeric properties [4].

However, there is one paper [14] in which the migration of an acyl radical is reported. Thus, camphoryl-phenyltriazine was obtained by the coupling of aminocamphor with diazobenzene, which was assigned structure (b) on the basis of the investigation of the decomposition products, even though structure (a) should have been assigned to it according to the method of preparing it.

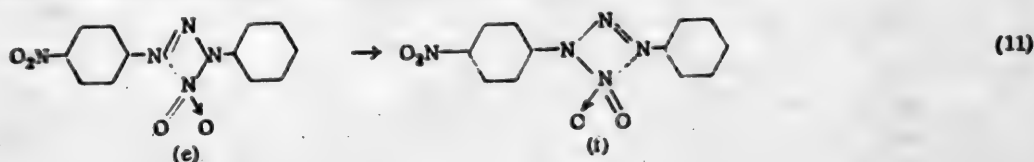


(b) forms the urea derivative (c) by treatment with phenyl isocyanate, which is transformed into compound (d) by heating in pyridine solution and by the action of light:

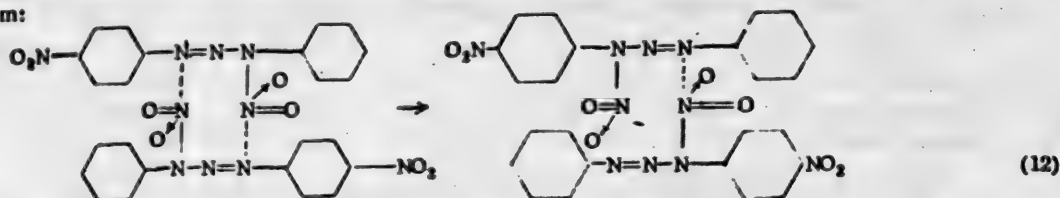


The movement of the phenylcarbamide group was detected by an investigation of the decomposition products and the sharply different optical properties of compounds (c) and (d).

The N-nitrotriazine obtained must have structure (e) according to the method of preparation. It can be supposed that the triazine undergoes an intramolecular redistribution of the electronic density by the action of the electron attracting group of the aromatic radical as a result of which the nitro group moves to the other nitrogen. A new triazine structure (f) is formed to which the decomposition products correspond.



With the presence of association of the molecules of N-nitrotriazines, the movement of the nitro group, viewed as an intermolecular interaction, becomes more probable. The scheme of such a movement explaining the appearance of compounds indicating the transposition of the nitro group in the reaction products can be shown simply in the following form:



Hydrolysis of the N-nitrotriazine occurring with the elimination of nitric acid and the formation of a new N-nitrotriazine by nitration with the nitric acid, appears less probable, since diazoamino compounds were not detected in the products of the reaction.

## EXPERIMENTAL

**1. Condensation of phenylnitraminic acid with diazo compounds.** A solution consisting of 1.60 g of the sodium salt of phenylnitraminic acid (0.01 mole), 25 ml of water, and 25-40 ml of a concentrated acetate buffer solution having a pH of 6 and containing 125 g of potassium acetate and 30 ml of glacial acetic acid in 200 ml of solution, was charged into a round-bottomed beaker fitted with a stirrer. The nitraminic acid was synthesized by the oxidation of the nitrosoamine of the corresponding diazo compound in alkaline medium [15]. The reaction beaker was cooled externally with ice so that the temperature of the solution was about 5°, and a solution of the diazo compound (0.01 mole) was added with rapid stirring over a 15-minute period. The diazo compound was prepared by the diazotization of 0.01 mole of the corresponding amine [16], freed from excess nitrous acid, and were used in the form of hydrochloric acid solutions containing 0.01 mole of the diazo compound and a 2-fold excess of hydrochloric acid, for the reaction.

In order to neutralize the acid introduced with the diazo compound solution (0.02 mole) and freed during condensation process (0.01 mole), it was necessary to add potassium bicarbonate or acetate. The reaction medium varied from pH 4.8 - pH 5.8. The control of the reaction medium was conducted on removed samples with a pH meter of the system GIPKh with glass electrodes [17].

The condensation was virtually complete after several hours; however, the diazo compound, giving a color reaction with R-salt, remained in solution for 2-3 days.

Soon after the addition of the diazo compound, the transparent reaction mixture became cloudy, and dark drops of a tarry substance appeared on the walls of the beaker and on the stirrer, the amount of which rapidly increased. This tar was partially converted into brownish flocs during the reaction, which settled to the bottom, or were found on the surface of the solution.

At the end of the reaction, the solution was filtered and the precipitate was washed with a large amount of water on the filter. As it was observed that the wash water from the precipitate was always rather green-yellow in color, it was collected separately and investigated.

The filtered and washed precipitate which was dried in a vacuum desiccator, was a dark-brown powder with darker inclusions visible to the naked eye. A sample under a microscope showed the heterogenous composition of the residue, and the absence of crystals in it. The residue, introduced on the end of a spatula into the flame of a burner, first melted with swelling, and then burst, leaving a carbonized mass. It was found to be partially soluble in ethyl alcohol, benzene, and chloroform, with the solutions being red or red-brown. Bubbles of a gas were evolved upon the solution of the crude residue in alcohol. The residue dissolved almost completely in acetone, coloring the solution brown. However, attempts to isolate the substance from solution in crystalline state were unsuccessful; upon cooling a saturated solution or upon diluting it with water, flocs tarry in character appeared.

The residue was treated in the cold with 0.5 N alkali, and a dark red solution was obtained. Solution was not complete even after prolonged treatment with a large amount of alkali. These alkaline solutions, however, also formed amorphous brown precipitates upon acidification.

\* The method was refined and supplemented by G. S. Salyamon



2. Isolation of the substance from the aqueous solution. The aqueous solution (filtrate, aqueous extract of the residue) which had a pH 6-7, was shaken with ether to remove the side products and then acidified with 10% hydrochloric acid to pH 3. The acidified solution was again extracted with ether, and the substance which colored the water solution was completely transposed into the ether layer. The ether was removed by evaporation at room temperature, and the crystals which formed were recrystallized many times from a mixture of alcohol and water.

3. Identification of the substances isolated from the aqueous solution. a) Substance obtained by the condensation of p-nitrophenyldiazonium with phenylnitraminic acid. The compound obtained was a light yellow crystalline substance with m.p. 110-111° which was poorly soluble in water and readily soluble in aqueous alkalis, alcohol, and ether. This compound burned explosively and gave a Liebermann reaction with a color characteristic for nitraminic acids. According to potentiometric titration data, it was a rather strong acid and had a molecular weight of about 184.

Found %: N 22.95, 23.00.  $C_6H_5O_4N_3$ . Calculated %: N 22.95.

According to all its properties, the compound obtained was identical with p-nitrophenylnitraminic acid which, according to literature data [18a] has an m.p. 110-111°. The identity of the compound isolated with p-nitrophenylnitraminic acid was proved by the absence of a depression in a mixed melting point with specially synthesized p-nitrophenylnitraminic acid. The latter was synthesized by the oxidation of the nitrosoamine of p-nitrophenylhydrazine in alkaline medium; its m.p. was 111-112°. The mixed melting point was 111-112°.

b) Substance obtained by the condensation of p-chloro-o-nitrophenyldiazonium with phenylnitraminic acid. The compound obtained was a light yellow crystalline substance with m.p. 107-108° which was poorly soluble in water and readily soluble in aqueous alkalis, alcohol, and ether. This compound burned explosively and gave a Liebermann reaction with a color characteristic for nitramines. According to potentiometric titration data, the compound was a rather strong acid and had a molecular weight of about 217.

Found %: N 19.55, 19.62.  $C_6H_3ClO_4N_3$ . Calculated %: N 19.31.

The identity of the compound obtained with p-chloro-o-nitrophenylnitraminic acid which has an m.p. 107-108° according to the literature data [18b], was proved by the absence of a depression in a mixed melting point with the specially synthesized nitraminic acid. The latter was synthesized by the oxidation of the corresponding nitrosoamine in alkaline medium; its m.p. was 108-109°. The mixed melting point was 108-109°.

c) Substance obtained by the condensation of p-nitro-o-chlorophenyldiazonium with phenylnitraminic acid. The compound obtained was a light yellow crystalline substance with m.p. 92-93° which was poorly soluble in water and readily soluble in aqueous alkalis, alcohol and ether. This compound burned explosively and gave a Liebermann reaction with a color characteristic for nitramines. Potentiometric titration data were the same as for the previous compound.

Found %: N 19.62, 19.52.  $C_6H_3ClO_4N_3$ . Calculated %: N 19.31.

According to all of its properties, the compound obtained was identical with p-nitro-o-chlorophenylnitraminic acid, which is unreported in the literature, and was synthesized by the authors by the oxidation of the nitrosoamine of the corresponding diazo compound in alkaline medium; m.p. 93-94°. The identity of the compounds obtained during the condensation reaction and the synthesized nitraminic acid, was proved by the mixed melting point, 93-94°.

4. Isolation of phenol. Phenol was isolated from the reaction mixture obtained by the condensation of the diazonium with phenylnitraminic acid. The reaction was conducted for 1-2 hours, and was stopped when the appearance of some of the tarry substance was first noticed in the reaction vessel. The entire reaction mixture including the tar, was heated almost to 100° in a period of several minutes; it was then steam distilled, after filtration and neutralization with 10% sodium hydroxide solution from pH 4-5 to pH 8. Phenol was detected in the condensate, approximately 300 ml, which was isolated in the usual manner in the form of tribromophenol and was identified by comparison with specially synthesized tribromophenol. The yield of phenol was approximately 30% of the theoretical.

5. Isolation of phenylazo-8-naphthol. The filtrate after the separation of the residue obtained as a result of the condensation of p-chloro-o-nitrodiazobenzene, was subjected to diazo coupling with an alkaline solution of 8-naphthol. The coupling was conducted in a weakly acidic medium (pH 5-6). The precipitated dye was filtered and recrystallized many times from a mixture of alcohol and water. According to its melting

point, the isolated dye was identical with phenylazo- $\beta$ -naphthol having an m.p. 130-131° [18c]; the melting point of the analogous compounds having a nitro or nitro and chloro group in the phenyl radical was considerably higher; namely, from 240-250°. Even though the isolated dye could not be purified from a difficultly separable impurity, and its melting point was somewhat lower than that of the specially synthesized phenylazo- $\beta$ -naphthol, nevertheless, according to a mixed melting point, it was phenylazo- $\beta$ -naphthol.

#### SUMMARY

1. The reaction between the diazo compounds, p-nitrodiazobenzene, p-nitro-o-chlorodiazobenzene, and p-chloro-o-nitrodiazobenzene and phenylnitraminic acid was studied, and the unstable diaryl-N-nitrotriazines, identified by their decomposition products, were detected for the first time.

2. The decomposition products of the diaryl-N-nitrotriazines were diazobenzene and a nitraminic acid with a nucleus corresponding to the diazo compound participating in the reaction, which indicates the transfer of the nitro group from one nitrogen of the triazine to the other, which was connected to the more negative radical.

3. The possible mechanism, which was the not-previously-encountered transfer of a nitro group in a N-nitrotriazine from one nitrogen to another, was discussed.

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Received February 3, 1953

PREPARATION, PROPERTIES, AND STRUCTURE OF COMENIC ACID  
(5-HYDROXY- $\gamma$ -PYRONE-2-CARBOXYLIC ACID)

G. A. Garkusha

Comenic acid is usually obtained by the decarboxylation of meconic acid [1, 2, 3, 4]. As was previously reported by the authors [6], its yield was 80% based upon purified dry meconic acid, and the comenic acid obtained, was not sufficiently pure. This depended upon the method of isolating meconic acid, the nature of which was related to the processing of the opium industry wastes, meconates, with dilute hydrochloric acid followed by purification by means of the potassium [7] or ammonium salts [8]. Mennel [8] employed dilute hydrochloric acid. Each of these methods has one or another drawback.

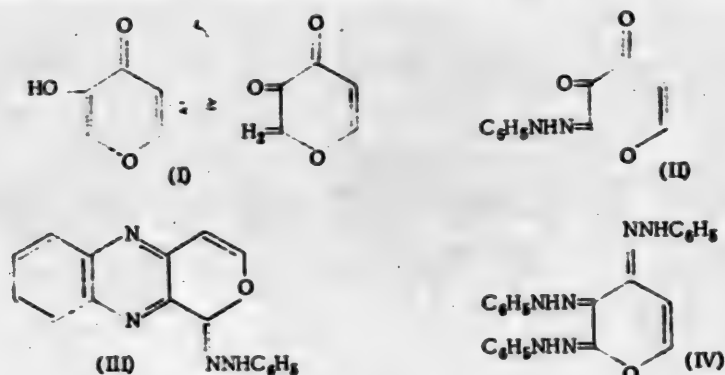
Since all of the methods for the isolation of meconic acid are rather laborious, the preparation of comenic acid directly from the meconates was of great interest. It was found that this could be accomplished by decarboxylating the meconates themselves. However, such a method was found to be applicable only for samples containing large amounts of meconic acids. Its application to the usual samples of meconates led to a strong tarring of the reaction mass, which in itself complicated the isolation of comenic acid and decreased its yield considerably. The starting products for the preparation of comenic acid were the usual samples and those from which meconic acid could not be isolated by known methods. It was found that, by using an initial treatment with HCl diluted 3:1, 2:1, or 1:1 (second figure is water) in the cold, comenic acid of a high degree of purity could be obtained from such samples of meconates, as well as from meconic acid. This method differs from the known methods of preparation of comenic acid in that it gives a product of a high degree of purity, as was determined by a determination of its melting point and the temperature of its decarboxylation.

The structure of comenic acid as 5-hydroxy- $\gamma$ -pyrone-2-carboxylic acid was proved by the following facts. The acid is a derivative of 3-hydroxy- $\gamma$ -pyrone, as this hydroxypyrene forms upon its decarboxylation [6, 9, 10]. It is also obtained by the decarboxylation of meconic acid, which is also a derivative of 3-hydroxy- $\gamma$ -pyrone (Thoms and Pietrulla [11]). Peratoner and Leone [12] showed that a small amount of comenic acid was formed on heating the sodium salt of 3-hydroxy- $\gamma$ -pyrone with carbon dioxide. A series of authors [3, 8, 13, 14, 15] showed that bromocomenic acid was obtained by the bromination of comenic or meconic acid, (1 mole bromine), as well as 6-iodocomenic acid [6] by their iodination. 6,6-Dibromocomenic acid was obtained by the action of 1 mole of bromine on 6-bromocomenic acid, or 2 moles of bromine on meconic acid. The structure of this acid as 3,6-dibromo-5-hydroxy- $\gamma$ -pyrone-2-carboxylic acid is not very probable, since it readily eliminates a bromine with the formation of 6-bromocomenic acid [8] when heated to 105°, or upon reduction with zinc or tin and hydrochloric acid. Its structure as 6,6-dibromocomenic acid is explained by the appearance of tautomers [16]. The formation of an  $\alpha$ -diketone group was proved by the preparation of a quinoxaline derivative, as well as the corresponding hydrazone. It is true that other authors could not duplicate these reactions.

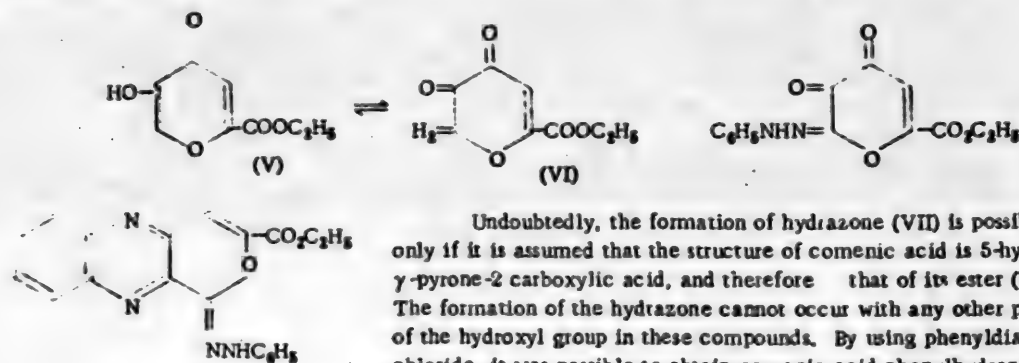
The hydrolysis of 6-bromocomenic acid leads to the preparation of 6-hydroxycomenic acid (5,6-dihydroxy- $\gamma$ -pyrone-2-carboxylic acid). A series of authors [5, 13, 15] showed that this hydrolysis proceeds smoothly. The same acid was obtained by the hydrolysis of 6-iodocomenic acid [6].

The transformation of comenic acid into comenamic acid, and the preparation of dihydroxypyridine from it, serves as proof of the structure of 3-hydroxy- $\gamma$ -pyrone and comenic acid [13, 17, 21, 22]. If the former is transformed into 3, 4- or 4, 5-dihydroxypyridine, then the position of the hydroxyl group in the hydroxypyrene only is demonstrated, but not in comenic or meconic acids, since the cited dihydroxypyridines can be formed from these acids if the hydroxyl group is in the ortho, or in the para position. For this reason, the attempt of Belonson [18] to prove the structure of comenic acid as 3-hydroxy- $\gamma$ -pyrone-2-carboxylic acid by the fact that he obtained 3,4-dihydroxypyridine from it, cannot stand up under criticism. This fact resulted in the erroneous conclusion on the structure of comenamic acid as 3,4-dihydroxypyridine-2-carboxylic acid, as well as the erroneous interpretation in the communication of Peratoner and Tamburello [19] who showed that the hydroxyl group was found in the para position in comenamic and comenic acids. The latter is confirmed in the communication of Jabara [20], who obtained 4,5-dihydroxy-2-methylpyridine from comenamic acid and kojic acid. It was also shown that 5-hydroxy-2-methyl- $\gamma$ -pyrone obtained

by the reduction of kojic acid, reacted with phenyldiazonium acetate to form "red crystals" of the azo compound (?). Apparently, its phenylhydrazone (II) was obtained by Peratoner and Carapelle [24] during an attempt to prepare the azo compound from 3-hydroxy- $\gamma$ -pyrone, which is only possible with occurrence of a keto-enol rearrangement (I). The quinoxaline derivative (III) of this phenylhydrazone (II) was obtained by reaction with *o*-phenylenediamine, and  $\gamma$ -pyrone trihydrazone (IV) by the condensation of (II) with 2 moles of phenylhydrazine.



Since Shimmrin and Challenger [26], quoting from [24] consider that hydroxypyrene phenylhydrazone was an authentically reported compound, we decided to test this premise. It was found that the reaction proceeded smoothly, but that the isolation of the hydrazone was hindered by its easy oxidizability especially in the moist state. By changing the reaction conditions and the procedure of isolating its products, 3-hydroxy- $\gamma$ -pyrone sulfonamidophenylhydrazone was obtained. Later, an attempt was made to prepare comenic acid phenylhydrazone based on the preparation of ethyl comenate phenylhydrazone, using phenyldiazonium acetate. This attempt was unsuccessful. For this reason the quinoxaline derivative (VIII) was obtained from hydrazone (VII):



Undoubtedly, the formation of hydrazone (VII) is possible only if it is assumed that the structure of comenic acid is 5-hydroxy- $\gamma$ -pyrone-2-carboxylic acid, and therefore that of its ester (V). The formation of the hydrazone cannot occur with any other position of the hydroxyl group in these compounds. By using phenyldiazonium chloride, it was possible to obtain comenic acid phenylhydrazone, as well as to isolate its acid sodium salt. The neutral salt was found to be unstable.

Finally, an indirect proof of the formation of these hydrazones of hydroxypyrene, comenic acid, and its ester, which is assured by the occurrence of tautomerism, is the absence of the latter in maltol, 3-hydroxy-2-methyl- $\gamma$ -pyrone, which does not react with phenyldiazonium, sulfonyl chloride, or amyl nitrite, and by the fact that its halogen derivative has not been obtained. The structure of maltol as 3-hydroxymethyl- $\gamma$ -pyrone was proved by its synthesis from 3-hydroxy- $\gamma$ -pyrone [25].

Therefore, the ability of comenic acid and its ethyl ester to form hydrazones agrees with its structure as 5-hydroxy- $\gamma$ -pyrone-2-carboxylic acid, and not 3-hydroxy- $\gamma$ -pyrone-2-carboxylic acid.

#### EXPERIMENTAL

1. Preparation of comenic acid. 100 g of pulverized meconates was added in portions with stirring at a temperature not higher than  $+10^\circ$  to 140 ml of hydrochloric acid (sp. gr. 1.19) and 70 ml of water. After stirring for 0.5 hours, the residue was filtered and washed with ice water. 80 g of this residue was added, at  $80-85^\circ$  within the reaction mixture, to 150 ml of hot dilute hydrochloric acid (1:1). The decarboxylation was over in 1 hour.

\* True, the authors did not characterize this compound.



and 80 ml of a 10% sodium chloride (C.P.) solution was added at 70°. The precipitate which formed after twenty-four hours was filtered and washed with ice water and alcohol. The weight of the air-dried residue was 40 g; that dried at 100-110°, 30 g.

40 g of the air-dried comenic acid was purified by mixing it with 560 ml of water and adding  $\text{NaHCO}_3$  in small portions (to 20 g) until the reaction was just acid (brown on Congo). The mixture was then heated to 70-75° until complete solution. The hot solution was filtered with carbon, and 160 g of sodium chloride was added to the filtrate, with stirring. The precipitated white crystals of the acid sodium salt were filtered and washed with the mother liquor and with alcohol. 45 g of the precipitate was mixed with an equal amount of water and 90 ml of hydrochloric acid, and then 45 ml of water was added. The comenic acid was filtered and washed with ice water and alcohol. The chlorides were removed by mixing the residue with water in a ratio of 1:2, followed by heating and cooling to 0°, and processing in the above manner. Dried at 120°, the snow-white crystals weighed 20 g; m.p. 273-274° (with tarring); 274-275° in a sealed capillary. Upon heating a layer of crystals on a cover glass in a Meker block melting point apparatus, they decarboxylated without leaving a residue and without changing color at 225-230° (the temperature was measured at the usual position of the thermometer in the apparatus). Aqueous and alcoholic solutions of ferric chloride were colored blood-red by the addition of the crystals.

2. Preparation of 3-hydroxy- $\gamma$ -pyrone phenylhydrazone. 5.5 g of anhydrous sodium acetate was added to a diazo solution prepared from 1.9 g of sodium nitrite, 2.4 g of aniline, 6 ml of HCl, and 12 ml water with ice. 2.8 g of 3-hydroxy- $\gamma$ -pyrone in 28 ml of water acidified with 1.2 ml of acetic acid was added at 0°. After 1 hour, a 5% hydrochloric acid solution was added at +5° to a violet reaction (Congo). The raspberry red precipitate was filtered and washed with ice water acidified with HCl (blue on Congo), the precipitate being kept covered, and then with water and ice. The blood-red crystals obtained were air dried. The yield was 5 g. The crystals were insoluble in petroleum ether and ethyl ether, and poorly soluble in xylene. Recrystallized from hot xylene, they had a broad melting point about 170° (176° according to Carapelle) with a change of color; at 190° the viscous mass carbonized.

When 1 g of crystals mixed with 5 ml of water acidified with HCl (blue on Congo), was treated with sulfur dioxide for 5 hours, they dissolved completely. Twenty-four hours later, yellow brown crystals insoluble in water, chloroform, and ether, and soluble in alcohol and acetone, came out.

3. Preparation of 3-hydroxy- $\gamma$ -pyrone-p-sulfamidophenylhydrazone. 3.5 ml of HCl (sp. gr. 1.19) and a solution of 0.85 g of sodium nitrite in 3 ml of water was added in 20 minutes at 0° to a mixture of 2.16 g of sulfanilamide and 12 ml of water. 3.5 ml of glacial acetic acid and 7.5 ml of 30% sodium acetate solution were added at -3° to the diazo solution (violet color on Congo). To the phenyldiazonium acetate at -3° was added a solution of 1.4 g of 3-hydroxy- $\gamma$ -pyrone in 20 ml of water with 3 ml of glacial acetic acid, and 3.5 ml of a 30% sodium acetate solution (red color on Litmus). A sample on filter paper was used to test the end of the reaction. The precipitate was filtered rapidly, washed with water and ice (without uncovering it) for 30 minutes, acidified with water and ice, and once more with water and ice. The residue, dried in the air, and then at 100°, weighed 1.8 g, which corresponded to 51% of the theoretical yield: bright red crystals with m.p. 260-265°, with the color of the melt changing to brown. It was insoluble in benzene, xylene, chloroform, and ether, difficultly soluble in alcohol; upon heating with acetone, solution occurred and a white precipitate formed.

0.7005 g substance: 0.5805 g  $\text{BaSO}_4$ , 0.3555 g substance: 0.409 ml  $\text{N}_2$  (21°, 740 mm) (according to Dumas).

0.2920 g substance: 0.341 ml  $\text{N}_2$  (20.5°, 741 mm) (with CuO). Found %: S 11.38; N 13.01, 13.24,

$\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_2\text{S}$ . Calculated %: S 10.8; N 14.25.

4. Preparation of ethyl comenate p-sulfamidophenylhydrazone. 17.2 g of sulfanilamide was added in portions with stirring at 0° to a mixture of 28 ml of HCl (sp. gr. 1.19), 96 ml of water, and 30 g of ice. After solution of most of the sulfanilamide, 30 g more of ice and a solution of sodium nitrite (7 g in 25 ml of water) was added, with continuous stirring until complete solution of the sulfanilamide, with the addition of 40 g more of ice. A solution of 18.5 g of ethyl comenate in 180 ml of 80% acetic acid was added to the diazo solution at +3°, and 100 ml of 30% sodium acetate, steadily, but not allowing the reaction to be violent, or the temperature to rise above +5°. A dark red precipitate of hydrazone was formed by the addition of 100 g of sodium chloride and acidification with dilute HCl (1:1) while the reaction mixture was cooled to -10°. The completion of precipitation was tested with a sample on filter paper. The precipitate was filtered immediately, washed with a saturated sodium chloride solution with ice (keeping the precipitate covered), and then with water and ice. Air dried, and then at 90-100° the dark red precipitate weighed 27.5 g which corresponded to 75% of the theoretical yield. The substance was insoluble in benzene, toluene, ether and petroleum ether: it was slightly soluble in chloroform, and gave a red solution;



it was slightly soluble in ethyl acetate, alcohol (absolute), and methanol (solutions colored yellow); it was readily soluble in pyridine and nitrobenzene (solutions colored yellow). Solution occurred upon heating with acetone, and a white precipitate formed. The crystals dissolved in nitrobenzene and precipitated with benzene, had a dark red color; dried, a raspberry. M.p. 173-175° (with carbonization).

0.2970 g substance: 0.4970 g CO<sub>2</sub>; 1.010 g H<sub>2</sub>O. 0.3380 g substance: 0.385 ml N<sub>2</sub> (23°, 734.5 mm).  
0.3760 g substance: 0.325 ml N<sub>2</sub> (22°, 73.8 mm). 0.2880 g substance: 0.256 ml N<sub>2</sub> (23°, 735 mm)  
(according to Dumas). 0.6140 g substance: 0.3910 g BaSO<sub>4</sub>. 0.7380 g substance: 0.4770 g BaSO<sub>4</sub>.  
Found %: C 45.64; H 3.81; N 9.4, 9.72, 9.92; S 8.74, 8.87. C<sub>12</sub>H<sub>13</sub>O<sub>7</sub>N<sub>3</sub>S. Calculated %: C 45.8;  
H 3.54; N 11.7, S 8.73.

5. Preparation of the quinoxaline derivative. 0.6 g of ethyl comenate p-sulfamidophenylhydrazone was dissolved in 4 ml of pyridine, acidified with 1 ml of glacial acetic acid, and mixed with a solution of 0.2 g of o-phenylenediamine in 2 ml of glacial acetic acid. After filtration of the solution which was heated to 80°, and cooling to 30°, a purple-red precipitate formed which was filtered and washed with methanol, ether, and benzene, and dried at 105°. 0.6 g of crystals were recrystallized from a mixture of pyridine and acetic acid. M.p. 290-295° (with carbonization).

0.4420 g substance: 0.599 ml N<sub>2</sub> (24°, 728 mm). 0.2170 g substance: 0.299 ml N<sub>2</sub> (23°, 728 mm).  
0.5770 g substance: 0.3195 g BaSO<sub>4</sub>. Found %: N 14.92, 15.22; S 7.6. C<sub>18</sub>H<sub>11</sub>O<sub>5</sub>N<sub>3</sub>S. Calculated %:  
N 15.95; S 7.3.

6. Preparation of comenic (5-hydroxy-γ-pyrone-2 carboxylic) acid phenylhydrazone. A solution of 2.6 g of sodium nitrite in 10.5 ml of water was added at 1-3° to a solution prepared from 2.8 g of aniline and 10.5 ml of HCl (sp. gr. 1.19), diluted with 26 ml of water. At the same time, 4.7 g of comenic acid was dissolved at 60-70° in 140 ml of water with the addition of 2.3 g of anhydrous potassium carbonate. This solution was cooled to +15° (the salt precipitated upon rapid cooling) and added to the diazo-solution. Then 60 g of sodium chloride was added, and the reaction mass was cooled to -5°. Dilute HCl (1:1) was added in portions, testing the completion of precipitation with a sample on filter paper. The black precipitate was filtered through a cloth filter (leaving it under the liquid) and washed, first with a saturated sodium chloride solution acidified with HCl (litmus) with pieces of ice, and then with ice water, and ether. Weight of the moist residue was 5.6 g. Weight in air-dried state, 3.5 g (black color with a red-violet sheen).

This 3.5 g of precipitate was mixed with 50 ml of water, and about 4.5 ml of 20% Na<sub>2</sub>CO<sub>3</sub> was added to a neutral reaction (yellow on bromothymol blue). The solution obtained was filtered with carbon, and 12 g of sodium nitrate was added to the filtrate with stirring until it dissolved. The hydrazone salt was precipitated with 100 ml of alcohol, filtered, and washed with a mixture of alcohol and ether (1:1). The sodium nitrate was washed out by one or two mixings with 70% alcohol; the completion of the washings was tested with diphenylamine. The weight of the air-dried precipitate was 2.5 g. The dried black crystals (red-violet sheen) had an m.p. of 195-198° (with tarring). The substance was insoluble in chloroform, benzene, ether, and ethyl acetate; it was slightly soluble in cold water, and to an extent of 1:40 in water heated to 45°. Upon heating with an excess of water to 60-70°, decomposition occurred continuing for several hours. The hydrazone was considerably more soluble in acetic acid and alcohol. Its acid sodium salt was red-violet, the neutral salt, orange. A solution of the neutral sodium salt decomposed completely upon standing for twenty-four hours at room temperature. The acid sodium salt of the hydrazone was more stable. It dissolved to an extent of 1:10 in water at 20°, and 1:5, at 45°. It was insoluble in alcohol, acetone, and ether. The acid sodium salt, precipitated from an aqueous solution with alcohol, did not have a sharp melting point: at 240°, the crystals became dark brown, at 250° they shrank and became grey, at 270° they blackened and, finally, at 300° and higher, the mass puffed up.

Because the red-violet solution of the acid sodium salt of the hydrazone was different from the orange solution of the neutral salt, it was possible to titrate it without an indicator (a recrystallized substance with m.p. 195-198° was used).

0.2800 g substance: 0.5650 g CO<sub>2</sub>; 0.08250 g H<sub>2</sub>O. 0.5260 g substance in 5.4 ml of water: 20.0 ml  
0.1 N HCl. 0.6820 g substance in 7.0 ml water: 26.0 ml 0.1 N HCl. Found %: C 55.01; H 3.28;  
M 264, 262. C<sub>12</sub>H<sub>13</sub>O<sub>5</sub>N<sub>3</sub>. Calculated %: C 55.3; H 3.08; M 260.

#### SUMMARY

1. A method for the preparation of comenic acid directly from the meconates is given.

2. The following compounds, unreported in the literature up to now, were obtained: 3-hydroxy- $\gamma$ -pyrone, ethyl comenate p-sulfamidophenyldiazone, and its quinoxaline derivative, and comenic acid phenyldiazone.

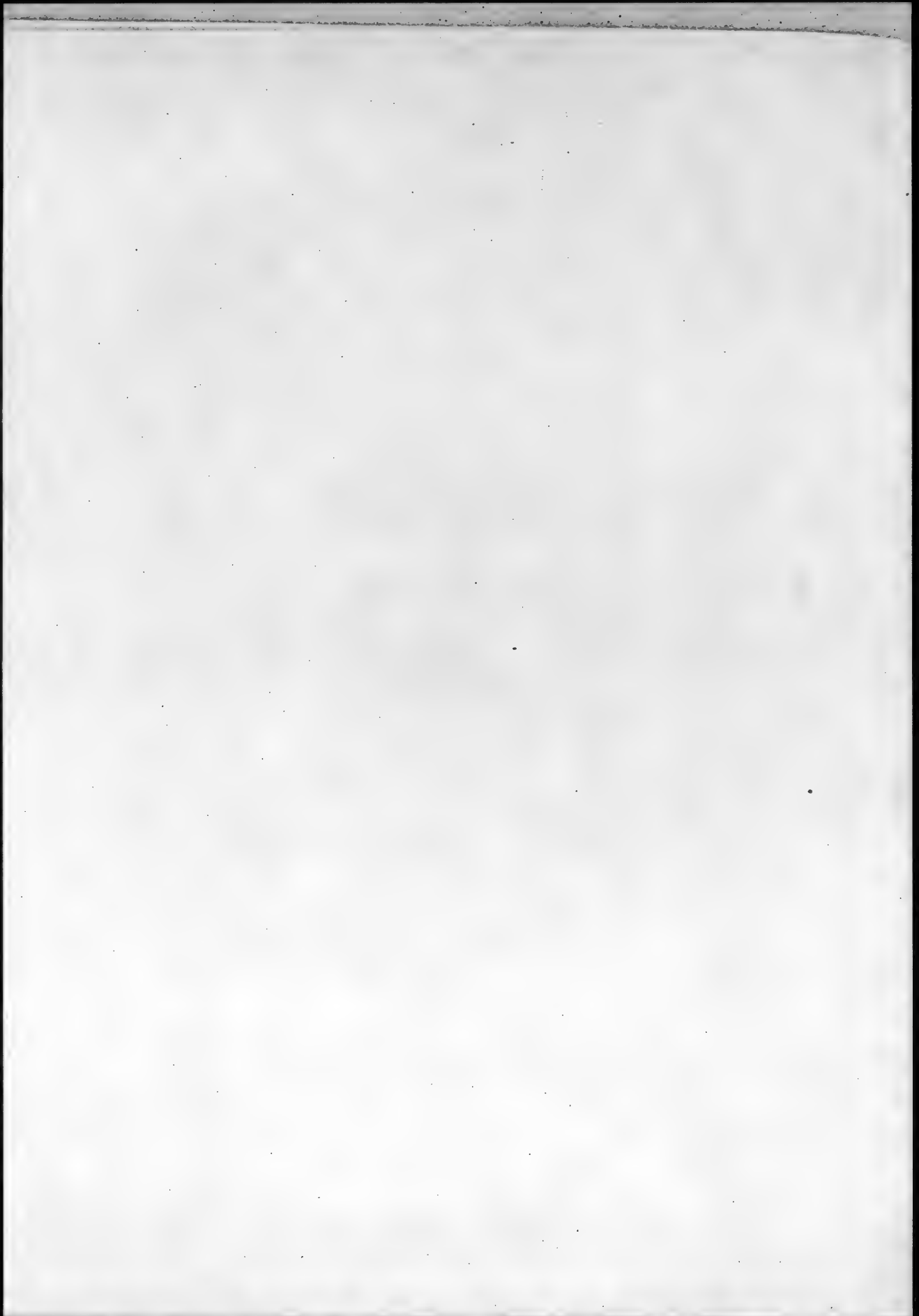
3. The structure of comenic acid was proved to be 5-hydroxy- $\gamma$ -pyrone-2-carboxylic acid by the obtaining of the above hydrazones.

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Received December 9, 1952.

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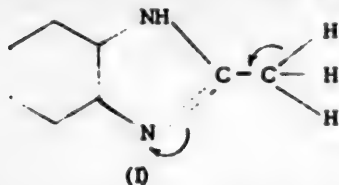


# REACTIVITY OF CERTAIN DERIVATIVES OF 2-METHYLBENZIMIDAZOLE

## I. REACTIONS OF THE METHYL GROUP HYDROGENS

B. A. Porai-Koshits and Kh. L. Muravich

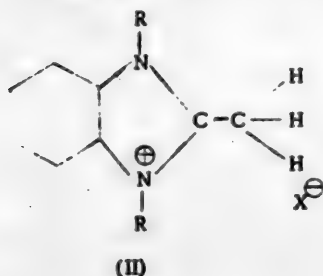
During the many years of investigating problems of the reactivity of organic compounds, A. E. Porai-Koshits studied especially thoroughly substances possessing active hydrogen atoms in methyl and methylene. The activity of the hydrogen atoms enables these substances to participate in condensation reactions with aldehydes, nitroso compounds, and diazo compounds. The relationship to these compounds characterizes the degree of reactivity of the hydrogen atoms of the methyl or methylene groups; the most active are those compounds which can condense not only with aldehydes and nitroso compounds, but can also participate in coupling reactions with diazo compounds. A. E. Porai-Koshits' investigations to determine the relation of the structure of substances possessing active hydrogen atoms in methyl and methylene groups, made possible the following summary in the form of a rule: if the methyl or methylene group is found in conjugation with the hetero atom, then its hydrogen atoms acquire an increased reactivity [1]. Therefore, the reactivity of the H atoms in these substances is due to the ability of the hetero atom to shift electrons.



2-Methylbenzimidazole (I) can be assigned to those compounds possessing reactive hydrogen atoms on the basis of A. E. Porai-Koshits' rule, and it is able to participate in condensation reactions with aldehydes, isatin, phenanthrenequinone, and phthalic anhydride [2].

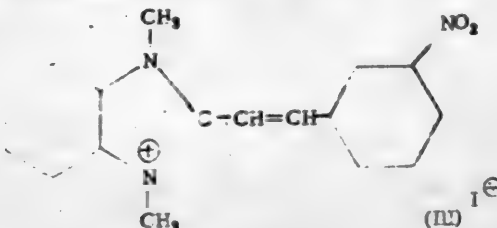
However, the reactivity of the hydrogen atoms of these substances is comparatively small, and the condensation reactions proceed only under forcing conditions. 2-Methylbenzimidazole is almost unable to react with nitroso- and diazo compounds [3]. The reason for the small reactivity of these compounds was seen by A. E. Porai-Koshits in the fact that the nitrogen of the group  $-C=N-$ , possessing an unshared pair of electrons, does not polarize the carbon-hydrogen bond strongly enough; on the other hand, this small polarization is weakened by the presence of an imino group whose unshared pair of electrons compensates the partial positive charge on the carbon atom in position 2.

It appeared possible to verify experimentally this explanation by synthesizing derivatives of 2-methylbenzimidazole in which the effect of the unshared pair of electrons on the nitrogen atom was eliminated, and to study the reactivity of the methyl groups of these compounds. The simplest method for blocking the unshared electron pair of one of the nitrogen atoms appeared to be the conversion of this compound into the quaternary derivative (II). The present investigation started with the synthesis of such a compound and the study of its properties. Initially, the methiodide derivative of 1,2-dimethylbenzimidazole was synthesized by the methylation of 2-methylbenzimidazole. The latter was obtained by heating *o*-phenylene diamine with acetic acid in a sealed tube.

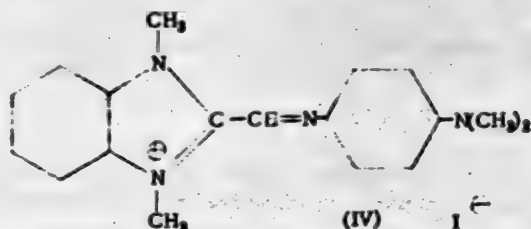


The quaternary compound obtained was found to be capable of reacting with *m*-nitrobenzaldehyde with a much greater ease than 2-methylbenzimidazole. The formation of the condensation product occurs even when the starting substances are boiled in alcoholic medium in the presence of piperidine.

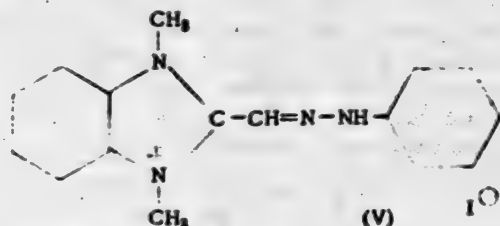
The reaction product, light yellow crystals, is 3-methyl-2-*m*-nitrostyrylbenzimidazole methiodide (III).



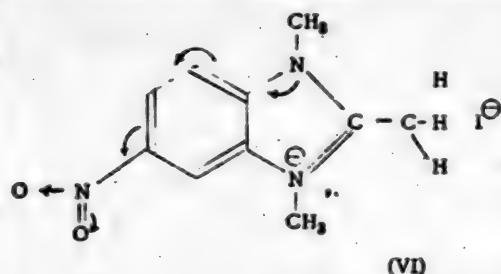
The condensation reaction with p-nitrosodimethylaniline proceeds under these conditions with the formation of violet crystals of the azomethine (IV). The latter possesses the characteristic properties of azomethines; i.e., it can be hydrolyzed upon heating with dilute hydrochloric acid. The aldehyde formed as the result of the



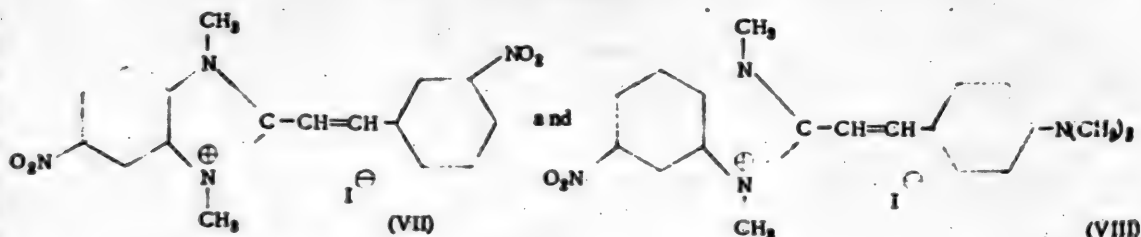
hydrolysis was converted into 3-methylbenzimidazol-2-aldehyde p-nitrophenylhydrazone methiodide (V) by reaction with p-nitrophenylhydrazone.



The ease with which the condensation products with aldehydes and nitro derivatives were formed indicated that the investigated compound was capable of participating in azo coupling reactions. However, all attempts to obtain the azo dye by coupling the methiodide derivative with diazo compounds from p-nitroaniline were unsuccessful. The reason for this behavior, evidently, is the presence of the second hetero atom. It is possible to assume that the unshared pair of electrons of the latter partially neutralizes the positive charge of the quaternary nitrogen. In order to prove this assumption experimentally, it was necessary in some way to remove the deactivating effect of the substituted imino group. For this purpose, an electrophilic group was introduced in conjugation with the second hetero atom. Initially, a nitro group introduced into position 5 (6) was chosen for this purpose.

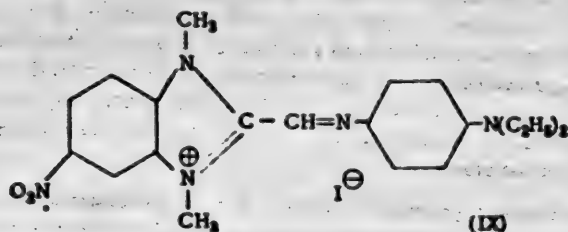


The synthesis of this compound (VI) was effected in two stages. 2-Methyl-5(6)-nitrobenzimidazole was obtained by the nitration of 2-methylbenzimidazole, which was then subjected to methylation in a sealed tube with methyl iodide [4]. The 2,3-dimethyl-5(6)-nitrobenzimidazole obtained readily reacted with m-nitro- and p-dimethylaminobenzaldehyde forming the condensation products (VII) and (VIII), the first of which, 3-methyl-2-m-nitroxyryl-5(6)-nitrobenzimidazole methiodide was a yellow, needle-like crystalline substance.



In addition to the condensation products with aldehydes, the corresponding azomethine (IX) was obtained by the condensation of 2,3-dimethyl-5(6)-nitrobenzimidazole methiodide with p-nitrosodimethylaniline.

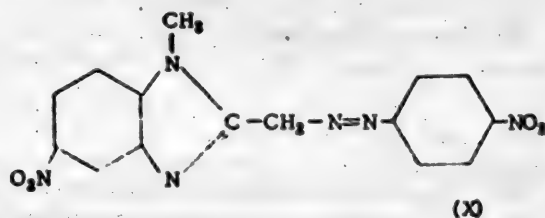




This product, which was a dark violet needle like substance with a green sheen, was readily hydrolyzed by the action of dilute acids with the formation of the corresponding aldehyde, which condenses with p-nitrophenylhydrazine to an orange hydrazone. The structure of the hydrazone remains undetermined up to now, since its composition according to the results of elementary analysis did not correspond to that calculated theoretically, and in addition, it did not contain iodine

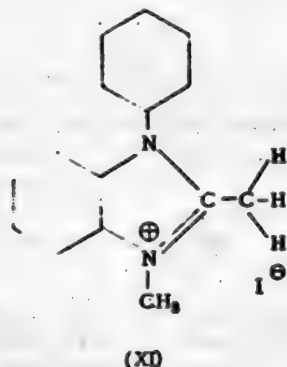
The greatest interest lies in the ability of 2-methyl-5(6)-nitrobenzimidazole methiodide to participate in azo coupling reactions with diazo compounds. The reaction proceeds in aqueous pyridine medium with the elimination of the methyl iodide occurring during the process of formation of the dye, which was indicated by the absence of a halogen in the dye obtained, and which was also confirmed by the determination of the elementary composition of the latter

The dye obtained from diazorized p-nitroaniline was a dark violet powder which was difficult to purify. After thorough purification, it can be obtained in the form of a dark green crystalline substance whose structure is expressed by the formula (X).



Establishing, therefore, the effect of the nitro group, a supplementary activation of the methyl group was attempted by other means. It seemed entirely possible to achieve the same effect by substituting the hydrogen of the imino group by some sort of an electrophilic group, as for example, a phenyl radical.

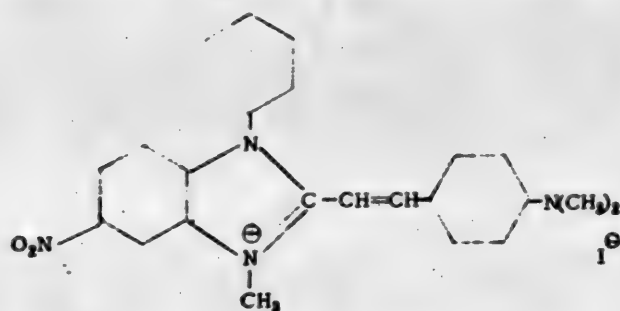
The synthesis of 1-phenyl-2-methylbenzimidazole was effected in several steps starting from o-nitrochlorobenzene. The latter was condensed with aniline by means of a method reported in the literature, but containing several changes. The o-nitrodiphenylamine was reduced with sodium sulfite to 2-aminodiphenylamine, from which 1-phenyl-2-methylbenzimidazole [5] was obtained by treatment with acetic anhydride and 4N hydrochloric acid. Two products were obtained upon methylating it: a white crystalline methiodide of 1-phenyl-2-methylbenzimidazole (XI), and the dark brown ones of its periodide (XII).



(XII)

It was possible to condense the first compound with p-dimethylaminobenzaldehyde. The reaction was conducted under the same conditions as all of the previous condensations. However, contrary to all expectations, the substance was found incapable of condensing with nitroso and diazo compounds. Therefore, the attempt to activate the molecule by replacing a hydrogen of the imino group with a phenyl radical did not lead to the expected results. In fact, according to the inability to condense with nitroso compounds, the activity of the compound was decreased. For this reason it seemed interesting to introduce a nitro group into position 5 of this compound, and to study the activity of the product obtained.

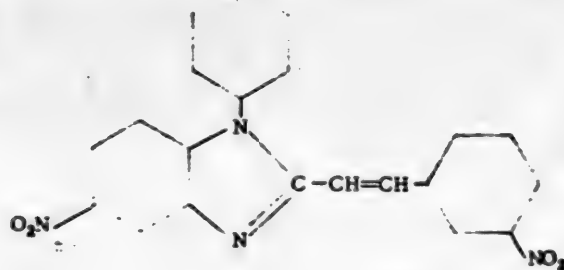
1-Phenyl-2-methyl-5-nitrobenzimidazole was synthesized by means of a method described in the literature [6]. It was found that the compound obtained condensed with p-dimethylaminobenzaldehyde only upon boiling in acetic anhydride; the structure of the condensation product corresponds to formula (XIII).



(XIII)

It is interesting to mention that this substance exists in two modifications: in the form of red-orange crystals with m.p. 245° or in the form of violet ones with a green sheen with the same melting point.

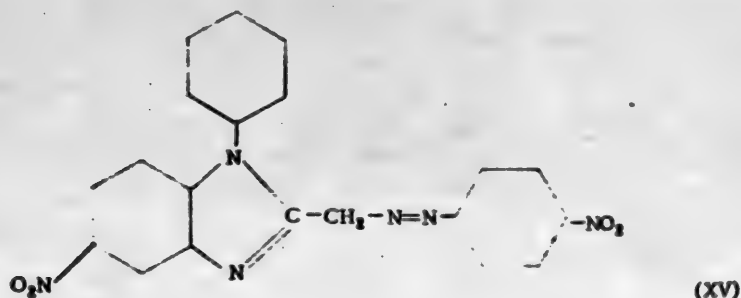
The reaction with m-nitrobenzaldehyde led to interesting results. The formation of the condensation product proceeded in alcoholic solution in the presence of piperidine and was accompanied by the elimination of methyl iodide. In order to prove this observation, 1-phenyl-2-methyl-5-nitrobenzimidazole ethiodide was synthesized, and was condensed with m-nitrobenzaldehyde under the same conditions. The condensation product was found to be identical with that obtained from the methiodide derivative, after thorough purification. The melting point, mixed melting point, as well as the analytical data, were found to be completely identical. Therefore, the structure of this compound may be represented by formula (XIV).



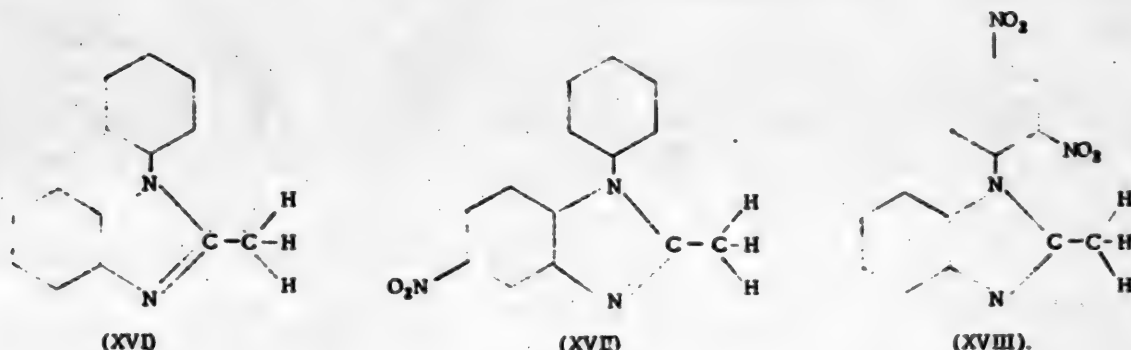
(XIV)

Condensation attempts with nitroso compounds were also unsuccessful in the given case. However, the azo coupling reaction in aqueous pyridine medium led to the formation of an azo dye. The formation of the dye was also accompanied by the loss of methyl iodide. The above reported method was used to prove the structure of the azo dye obtained; i.e., a coupling was effected with the ethiodide derivative. A product, completely identical with the dye obtained from the methiodide compound was obtained. The structure of the dye, therefore, can be represented by the formula (XV).

In addition to the methods for the activation of the hydrogen atoms of the methyl group of 2-methylbenzimidazole reported above and consisting mainly of the conversion of the nitrogen atom to an onium state, it seemed of interest to attempt this activation by introducing electrophilic groups into the imidazole ring. These groups should



have increased the activity of the methyl group hydrogens by shifting the electrons of the nitrogen atoms toward themselves. The following were chosen as examples: 1-phenyl-2-methylbenzimidazole (XVI), 1-phenyl-2-methyl-5-nitrobenzimidazole (XVII), and 1-(2,4-dinitro)-phenyl-2-methylbenzimidazole (XVIII)\*.



Since there are no data on tests of the activity of these compounds by condensation with aldehydes or nitroso compounds, condensation experiments were conducted with these compounds. The ability to react under mild conditions was of interest as a means of determining the degree of their activity. However, not even one of these compounds was able to react with aldehydes or nitroso compounds in low boiling solvent media. Even the replacement of an imino group hydrogen by such a strong acidifying radical as dinitro phenyl did not lead to a noticeable increase in the activity of the methyl group.

#### EXPERIMENTAL

**1. 3-Methyl-2-m-nitrostyrylbenzimidazole methiodide.** A mixture of 2.9 g of 1,2-dimethylbenzimidazole methiodide, 1.5 g of m-nitrobenzaldehyde, 10 ml ethyl alcohol were refluxed for 1 hour. The reaction was catalyzed with 5-10 drops of piperidine which was added before the heating. The starting substances first dissolved, and then as the heating progressed, a yellow condensation product precipitated from the solution. This product was purified by treating it with hot alcohol, and by recrystallization from water. The yield of the product was 1.7 g which is 40% of the theoretical. The product is a pale yellow crystalline substance with m.p. 293°.

0.1101 g. subs. 9.8 ml N<sub>2</sub> (24°, 757 mm). 0.1154 g subs. 10.1 ml N<sub>2</sub> (24°, 757 mm). 0.2490 g subs. 0.1382 g AgI 0.2252 g subs. 0.1250 g AgI. Found % N 10.2, 10.0; I 30.0, 30.02. C<sub>17</sub>H<sub>14</sub>O<sub>2</sub>N<sub>3</sub>I. Calculated %: N 9.97; I 30.16.

**2. Azomethine from 1,2-Dimethylbenzimidazole methiodide and p-Nitrosodimethylaniline.** The condensation of 1,2-dimethylbenzimidazole methiodide with p-nitrosodimethylaniline was conducted under conditions essentially analogous to the above. The condensation product separated from the solution after cooling in the form of violet crystals with m.p. 270°. It crystallized from methyl or ethyl alcohol.

\* See the experimental section for the synthesis of 1-(2,4-dinitro)-phenyl-2-methylbenzimidazole.

0.1120 g subs.: 13.1 ml  $N_2$  (25°, 754 mm). 0.1092 g subs.: 12.8 ml  $N_2$  (25°, 754 mm). 0.2133 g subs.: 0.1188 g AgI. 0.2120 g subs.: 0.1178 g AgI. Found %: N 13.49, 13.46; I 30.13, 30.05.  $C_{13}H_{11}N_4I$ . Calculated %: N 13.3; I 30.24.

3. Cleavage of the azomethine: 1-methylbenzimidazole-2-aldehyde p-nitrophenylhydrazone. 0.42 g of the azomethine (substance obtained in the previous experiment) was dissolved by heating in 25 ml of 3% hydrochloric acid. The hydrolysis of the azomethine proceeded with the solution turning yellow. The aldehyde could not be isolated from the solution. Its presence was proved by the action of p-nitrophenylhydrazine. For this purpose the calculated amount of p-nitrophenylhydrazine dissolved in 25 ml of 3% hydrochloric acid was added to the solution. A yellow flocculent precipitate formed upon boiling. The hydrazone was recrystallized from 50% acetic acid; it was a yellow crystalline substance with a bluish sheen with m.p. 270°.

0.1122 g subs.: 15.8 ml  $N_2$  (24°, 764 mm). 0.1236 g subs.: 17.3 ml  $N_2$  (24°, 764 mm). 0.1760 g subs.: 0.0939 g AgI. 0.1538 g subs.: 0.0819 g AgI. Found %: N 16.23, 16.13; I 28.89, 28.8.  $C_{13}H_{11}O_2N_4I$ . Calculated %: N 15.99; I 28.99.

4. Attempts to couple 1,2-dimethylbenzimidazole methiodide with p-nitrophenyldiazonium. Attempts at azo coupling were made in water, glacial acetic acid, and pyridine. The formation of an azo dye did not occur in any case.

5. 1-Methyl-2-dimethylaminostyryl-5(6)-nitrobenzimidazole methiodide. 1.65 g of 1,2-dimethyl-5(6)-nitrobenzimidazole and 0.75 g of p-dimethylaminobenzaldehyde were dissolved with heating in 20 ml of ethyl alcohol and after the addition of 4-5 drops of piperidine, refluxed for 1 hour. Almost immediately after the start of the boiling, the solution became intensely red, and soon, a dark red precipitate began to come out. The yield of the crude product was 1.25 g which is 55.5% of the theoretical. The product was recrystallized from methyl alcohol or from 80% acetic acid; it was a dark-red, finely crystalline substance with m.p. 248°.

0.1034 g subs.: 10.9 ml  $N_2$  (24°, 762 mm). 0.0979 g subs.: 10.4 ml  $N_2$  (24°, 762 mm). 0.1428 g subs.: 0.0720 g AgI. 0.2424 g subs.: 0.1230 g AgI. Found %: N 12.1, 12.1; I 27.31, 27.59.  $C_{19}H_{21}O_2N_4I$ . Calculated %: N 12.07; I 27.37.

6. 1-Methyl-2-m-nitrostyryl-5(6)-nitrobenzimidazole methiodide. This compound was obtained by means of an analogous condensation of the methiodide derivative with m-nitrobenzaldehyde. 1.1 g of the condensation product was obtained from 1.65 g of the methiodide, which is 50% of the theoretical. The product was recrystallized from 80% acetic acid. Yellow, fine needles with m.p. 265° were obtained.

0.0896 g subs.: 9.4 ml  $N_2$  (24°, 760 mm). 0.1010 g subs.: 10.6 ml  $N_2$  (24°, 760 mm). 0.1608 g subs.: 0.0814 g AgI. 0.2170 g subs.: 0.1090 g AgI. Found %: N 12.05, 12.1; I 27.36, 27.2.  $C_{19}H_{19}O_4N_4I$ . Calculated %: N 12.0; I 27.25.

7. Azomethine from 1,2-dimethyl-5(6)-nitrobenzimidazole methiodide and p-nitrosodiethylaniline. The preparation of the azomethine from 1,2-dimethyl-5(6)-nitrobenzimidazole methiodide and p-nitrosodiethylaniline was effected under the same conditions as in the previous condensation. After cooling the solution, 1.1 g of violet crystals separated (from 1.65 g of the starting methiodide). This is a yield of 45% of the theoretical. After recrystallization from ethyl alcohol, the product was obtained in the form of shiny dark green needles with m.p. 202°.

0.1101 g subs.: 13.7 ml  $N_2$  (24°, 764 mm). 0.1012 g subs.: 12.7 ml  $N_2$  (24°, 764 mm). 0.1832 g subs.: 0.0873 g AgI. 0.2010 g subs.: 0.0954 g AgI. Found %: N 14.33, 14.45; I 25.76, 25.66.  $C_{18}H_{23}O_2N_4I$ . Calculated %: N 14.2; I 25.76.

8. Hydrolysis of the azomethine. Preparation of the hydrazone. 1.1 g of the azomethine obtained in the previous experiment was dissolved with heating in 50 ml of hydrochloric acid. 0.3 g of p-nitrophenylhydrazine dissolved in 3% hydrochloric acid was added to the yellow solution. The mixture was boiled for 15 minutes. An orange flocculent precipitate formed during the boiling. After recrystallization from acetic acid, the product was obtained in the form of fine needles with m.p. 270°, which reversibly change color upon heating. It did not contain iodine.

9. Coupling of 1,2-dimethyl-5(6)-nitrobenzimidazole methiodide with p-nitrophenyldiazonium. 3.3 g of the methiodide derivative was dissolved in 300 ml of water, 40 ml of pyridine was added, and a solution of p-nitrophenyldiazonium obtained by diazotizing 1.4 g of p-nitroaniline in the usual manner, was added gradually to this solution, cooled to +5°. A dark precipitate formed with the addition of the diazo solution, which was allowed to settle at the end of the reaction. The yield of the crude product was 2.4 g, which is 50% of the theoretical. To purify the product, the impurities were extracted with petroleum ether in a Soxhlet apparatus. The

residue after the extraction was boiled with a small amount of methyl alcohol for a final removal of the impurities which were more soluble in the alcohol than the dye. The product was converted into a crystalline state during this processing, while the color changed from violet to dark green. The dye was then dissolved in pyridine, filtered, and precipitated with water. The melting point of the pure product was 266°. The dye was readily soluble in pyridine and dioxane with an intense violet color. It was partially soluble in alcohol and acetone with a dark red color.

0.1126 g subs.: 24.5 ml N<sub>2</sub> (24°, 754 mm). 0.1948 g subs.: 22.9 ml N<sub>2</sub> (24°, 754 mm). Found %: N 24.8, 24.91. C<sub>18</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub>. Calculated %: N 24.71.

**10. Preparation of o-Nitrophenylene diamine.** 31.5 g of o-nitrochlorobenzene was refluxed with 40 g of aniline, using an air condenser for 3 hours. The reaction product was poured into water, acidified with hydrochloric acid, and the unreacted o-nitrochlorobenzene was steam distilled. The reaction product separated from the remaining mixture after cooling in the form of a black precipitate from which o-nitrodiphenylamine was removed by extraction with petroleum ether in a Soxhlet apparatus. Pure o-nitrodiphenylamine precipitated from the petroleum ether upon cooling in the form of orange crystals with m.p. 75°.

**11. Phenyl-o-phenylenediamine (o-Aminodiphenylamine).** A mixture of 5 g of o-nitrodiphenylamine and 20 g of sodium sulfide in 50 ml of ethyl alcohol was refluxed for 1.5-2 hours with efficient stirring. The mixture was then diluted with water, acidified with hydrochloric acid, and boiled to precipitate the sulfur. After filtration of the sulfur, o-aminodiphenylamine was precipitated with ammonia. It melted at 79-80° after recrystallization from a mixture of alcohol and water.

**12. 1-Phenyl-2-methylbenzimidazole methiodide.** 1-Phenyl-2-methylbenzimidazole, obtained by means of a method reported in the literature [7], was heated with an equimolecular amount of methyl iodide in the presence of methyl alcohol for 4 hours in a sealed tube at 140°. The contents of the tube crystallized in the form of a light brown mass. The reaction product was treated with warm methyl alcohol in order to separate 1-phenyl-2-methylbenzimidazole methiodide. The insoluble part was a brown crystalline periodide. The methiodide was precipitated from the alcoholic solution with ether. It was obtained in the form of white, needle-like crystals with m.p. 217-218°.

0.1200 g subs.: 8.7 ml N<sub>2</sub> (24°, 752 mm). 0.1775 g subs.: 12.6 ml N<sub>2</sub> (24°, 752 mm). 0.1470 g subs.: 0.0982 g AgI. 0.1880 g subs.: 0.1258 g AgI. Found %: N 8.24, 8.07; I 36.33, 36.19. C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>I. Calculated %: N 8.00; I 36.28.

**13. 1-Phenyl-2-p-dimethylaminostyrylbenzimidazole methiodide.** 1.75 g of 1-phenyl-2-methylbenzimidazole methiodide and 0.75 g of p-dimethylaminobenzaldehyde were boiled with several drops of piperidine in ethyl alcohol solution for 1 hour. The solution gradually became intense red. After cooling and dilution with water, the impure reaction product had the form of an oily mass. After treatment with benzene, the product solidified in the form of a red powder which was obtained in the form of bright red needle-like crystals with m.p. 179-180° after recrystallization from water. The yield of the product was 1.5 g after treatment with benzene, which is 62.2% of the theoretical.

0.1182 g subs.: 9.1 ml N<sub>2</sub> (24°, 762 mm). 0.1074 g subs.: 8.3 ml N<sub>2</sub> (24°, 762 mm). 0.2355 g subs.: 0.1150 g AgI. 0.2014 g subs.: 0.0980 g AgI. Found %: N 8.85, 8.9; I 26.4, 26.32. C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>I. Calculated %: N 8.7; I 26.4.

**14. Attempts to Condense 1-Phenyl-2-methylbenzimidazole methiodide with p-Nitrosodimethylaniline.** An attempt to condense the starting products in alcoholic solution in the presence of piperidine was unsuccessful. Upon diluting the solution with ether, the starting imidazole was recovered.

**15. Attempted Azo Coupling of 1-Phenyl-2-methylbenzimidazole methiodide.** Attempts were made to azo couple with p-nitrophenyldiazonium in alcohol, glacial acetic acid, and pyridine. However, these attempts did not lead to positive results.

**16. 1-Phenyl-2-p-dimethylaminostyryl-5-nitrobenzimidazole methiodide.** 2 g of 1-phenyl-2-methyl-5-nitrobenzimidazole methiodide, synthesized according to a literature method [6] and 0.75 g of p-dimethylaminobenzaldehyde was boiled for 1 hour with 10 ml of acetic anhydride. The solution acquired a claret color with the boiling. After cooling, violet needles with a green sheen separated from the solution. The yield of the product was 1.5 g which is 56.4% of the theoretical. Upon recrystallization from acetic anhydride, orange-red crystals with m.p. 245°, or violet needles with a green sheen with the same melting point were obtained. The same result was obtained upon recrystallization from alcohol. It must, however, be mentioned that the violet crystals are easily obtained from alcohol, and the orange-red from acetic anhydride.



Analysis of the red product:

0.1104 g subs.: 10.5 ml  $N_2$  (24°, 752 mm). 0.1088 g subs.: 10.3 ml  $N_2$  (24°, 752 mm). 0.1478 g subs.: 0.0667 g AgI. 0.2110 g subs.: 0.0940 g AgI. Found %: N 10.81, 10.76; 124.41, 24.09.  $C_{24}H_{23}O_2N_4$ . Calculated %: N 10.66; 124.14.

17. Condensation with m-Nitrobenzaldehyde. The condensation of 2 g of 1-phenyl-2-methyl-5-nitrobenzimidazole methiodide with an equimolecular amount of m-nitrobenzaldehyde was effected in alcohol in the presence of piperidine. A yellow precipitate formed upon boiling, whose yield was 1.2 g which is 61.5% of the theoretical. For purification, the product was treated with hot alcohol and benzene, then dissolved in pyridine, and precipitated with water. The purified product melted at 220° (with decomposition).

0.1120 g subs.: 0.2122 g  $CO_2$ ; 0.0370 g  $H_2O$ . 0.9991 g subs.: 12.5 ml  $N_2$  (23°, 769 mm). 0.1010 g subs.: 12.8 ml  $N_2$  (25°, 770 mm). Found %: C 65.1; H 3.7; N 14.7, 14.63.  $C_{21}H_{14}O_4N_4$ . Calculated %: C 65.28; H 3.62; N 14.5.

18. 1-Phenyl-2-methyl-5-nitrobenzimidazole ethiodide. 5 g of 1-phenyl-2-methyl-5-nitrobenzimidazole was heated with 2 ml of ethyl iodide and 5 ml of ethyl alcohol for 4 hours at 140° in a sealed tube. The reaction product, a brown crystalline mass, was treated with methyl alcohol; the ethiodide separated from the solution upon the addition of ether in the form of yellow crystals with m.p. 266°.

0.2032 g subs.: 18.3 ml  $N_2$  (23°, 760 mm). 0.1864 g subs.: 17 ml  $N_2$  (23°, 760 mm). 0.2127 g subs.: 0.1220 g AgI. 0.3039 g subs.: 0.1736 g AgI. Found %: N 31.0, 30.89; 110.39, 10.52.  $C_{16}H_{12}O_2N_4$ . Calculated %: N 31.06; 110.27.

19. Condensation of the Ethiodide with m-Nitrobenzaldehyde. 1.6 g of 1-phenyl-2-methyl-5-nitrobenzimidazole ethiodide was condensed with 0.6 g of m-nitrobenzaldehyde, keeping the conditions of the condensation of the methiodide with m-nitrobenzaldehyde. The purified condensation product had the same melting point (220°). A mixed sample of both products melted at 220°.

0.1214 g subs.: 0.2900 g  $CO_2$ ; 0.0412 g  $H_2O$ . 0.1100 g subs.: 13.8 ml  $N_2$  (24°, 768 mm). Found %: C 65.2; H 3.79; N 14.6.  $C_{21}H_{14}O_4N_4$ . Calculated %: C 65.28; H 3.62; N 14.5.

20. Attempts to Condense 1-Phenyl-2-methyl-5-nitrobenzimidazole methiodide with p-Nitrosodimethylaniline. An attempt was made to condense the above products in alcohol with the addition of piperidine or sodium carbonate. Neither in the first or the second case was the expected product obtained. The starting imidazole was recovered from the solution by means of ether.

21. Coupling of 1-Phenyl-2-methyl-5-nitrobenzimidazole methiodide with p-Nitrophenyldiazonium. 4 g of the methiodide was dissolved in 500 ml of water and 40 ml of pyridine. A diazo solution prepared from 1.4 g of p-nitroaniline and neutralized with sodium acetate, was added dropwise to this solution at 0°. A violet color appeared, and the formation of a dark precipitate occurred. The precipitate was allowed to settle and was filtered. To remove the impurities from the dye, it was extracted with petroleum ether, and then boiled with ethyl alcohol. A partial solution of the dye occurred, but the main part of the dye remained undissolved and was converted to the crystalline state, as a result of which it changed from violet to dark green. After such treatment, the dye was dissolved in pyridine, and then precipitated from the solution with water. The pure product melted at 292°.

0.1012 g subs.: 0.2225 g  $CO_2$ ; 0.0320 g  $H_2O$ . 0.0676 g subs.: 12.3 ml  $N_2$  (23°, 762 mm). 0.0824 g subs.: 15.1 ml  $N_2$  (23°, 762 mm). Found %: C 60.0; H 3.53; N 21.04, 21.18.  $C_{20}H_{14}O_4N_4$ . Calculated %: C 60.12; H 3.5; N 20.82.

22. Coupling of 1-Phenyl-2-methyl-5-nitrobenzimidazole ethiodide with p-Nitrophenyldiazonium. The coupling of the ethiodide was conducted under the same conditions as that of the methiodide. The product obtained melted at 292° after thorough purification.

0.1104 g subs.: 0.2428 g  $CO_2$ ; 0.0355 g  $H_2O$ . 0.0987 g subs.: 18 ml  $N_2$  (23°, 762 mm). Found %: C 60.02; H 3.59; N 21.09.  $C_{20}H_{14}O_4N_4$ . Calculated %: C 60.12; H 3.5; N 20.89.

23. 2-Amino-2,4-dinitrodiphenylamine. 20.2 g of dinitrochlorobenzene was mixed with 10.8 g of o-phenylene diamine. 8.2 g of sodium acetate and 50 ml of ethyl alcohol were added to the mixture which was then boiled on the water bath for 1 hour. A crystalline precipitate formed upon boiling which consisted of a mixture of red rhombic and yellow needle-like crystals. After cooling, the precipitate was filtered and washed with hot water to remove the sodium chloride formed. The yield of the condensation product was 22 g which is 80.5% of the theoretical. The product was recrystallized from alcohol and glacial acetic acid. Yellow needles formed upon rapid cooling in the first, and in the second case, a mixture of yellow and red crystals upon slow cooling. The yellow,

as well as the red product melted at 151°. The yellow substance reddened when close to the melting point.

**Analysis of the red product:**

0.1156 g subs.: 0.2220 g CO<sub>2</sub>; 0.0391 g H<sub>2</sub>O. 0.1248 g subs.: 0.2395 g CO<sub>2</sub>; 0.0435 g H<sub>2</sub>O. 0.1181 g subs.: 10.9 ml N<sub>2</sub> (24°, 764 mm). 0.1205 g subs.: 21.4 ml N<sub>2</sub> (24°, 764 mm). Found %: C 52.4, 52.37; H 3.78, 3.81; N 20.52, 20.6. C<sub>12</sub>H<sub>10</sub>O<sub>4</sub>N<sub>4</sub>. Calculated %: C 52.55; H 3.65; N 20.43.

**24. 2-Acetylamino-2,4-dinitrodiphenylamine.** 2.75 g of 2-amino-2,4-dinitrodiphenylamine was boiled for a short time with 2 ml of acetic anhydride and 10-15 ml of acetic acid. The substance went into solution upon boiling, from which bright yellow, scaly crystals separated after cooling. The yield of the product was 2.9 g which is 92% of the theoretical; m.p. 235°.

It was hydrolyzed upon prolonged boiling with 4N hydrochloric acid with the formation of the hydrochloride and, of the starting 2-amino-2,4-dinitrodiphenylamine. The latter was a yellow crystalline substance with m.p. 147°. It was recrystallized from dilute hydrochloric acid; even boiling with water converted it into the starting 2-amino-2,4-dinitrodiphenylamine.

**Analysis of the acetyl derivative:**

0.1218 g subs.: 0.2294 g CO<sub>2</sub>; 0.0403 g H<sub>2</sub>O. 0.1065 g subs.: 0.2031 g CO<sub>2</sub>; 0.0357 g H<sub>2</sub>O. 0.1182 g subs.: 18.2 ml N<sub>2</sub> (25°, 762 mm). 0.1202 g subs.: 18.6 ml N<sub>2</sub> (25°, 762 mm). Found %: C 51.4, 51.32; H 3.7, 3.75; N 17.78, 17.9. C<sub>14</sub>H<sub>12</sub>O<sub>5</sub>N<sub>4</sub>. Calculated %: C 51.53; H 3.58; N 17.7.

**25. 2-Diacetylamino-2,4-dinitrodiphenylamine.** 5.5 g of 2-amino-2,4-dinitrodiphenylamine was heated with 20 ml of acetic anhydride for 2 hours at 180° in a sealed tube. The contents of the tube were a yellow crystalline substance after cooling. The yield of the product was 6.1 g which is 85.2% of the theoretical. After recrystallization from alcohol, the product was obtained in the form of light yellow, shiny platelets with m.p. 189° (with decomposition). Even upon short boiling in alcoholic solution in the presence of several drops of piperidine, the product eliminated one acetyl group, and was transformed into the monoacetyl derivative.

0.1156 g subs.: 0.2265 g CO<sub>2</sub>; 0.0423 g H<sub>2</sub>O. 0.1311 g subs.: 0.2569 g CO<sub>2</sub>; 0.0447 g H<sub>2</sub>O. 0.1212 g subs.: 16.8 ml N<sub>2</sub> (25°, 756 mm). 0.1014 g subs.: 13.8 ml N<sub>2</sub> (24°, 756 mm). Found %: C 53.46, 53.47; H 4.09, 3.82; N 15.85, 15.55. C<sub>14</sub>H<sub>12</sub>O<sub>5</sub>N<sub>4</sub>. Calculated %: C 53.63; H 3.91; N 15.6.

**26. 1-(2,4-Dinitro)-phenyl-2-methylbenzimidazole.** 3 g of the diacetyl derivative was heated with 20 ml of 4N hydrochloric acid for 2 hours at 170° in a sealed tube. After opening the tube, the transparent solution was poured into a beaker, diluted with 50 ml of water, and the reaction product precipitated with ammonia. The yellow precipitate was filtered, dried, and recrystallized from benzene. The yield of the crude product was 2.35 g, which is 94% of the theoretical. After recrystallization, the product was obtained in the form of yellow shiny platelets with m.p. 179°. The product was also recrystallized from dilute alcohol.

0.1244 g subs.: 0.2562 g CO<sub>2</sub>; 0.0389 g H<sub>2</sub>O. 0.1155 g subs.: 0.2377 g CO<sub>2</sub>; 0.0372 g H<sub>2</sub>O. 0.1048 g subs.: 17.2 ml N<sub>2</sub> (23°, 762 mm). 0.1136 g subs.: 18.7 ml N<sub>2</sub> (23°, 762 mm). Found %: C 56.2, 56.1; H 3.5, 3.6; N 18.90, 19.03. C<sub>14</sub>H<sub>10</sub>O<sub>4</sub>N<sub>4</sub>. Calculated %: C 56.39; H 3.36; N 18.79.

As stated above, 1-(2,4-dinitro)-phenyl-2-methylbenzimidazole, in spite of the presence of a strong electrophilic residue (dinitrophenyl) in the molecule, was found to be incapable of participating in condensations with aldehydes and nitroso compounds under various conditions.

**SUMMARY**

1. The main factor in the increase of the activity of a methyl group is the positive charge on the nitrogen atom in conjugation with this group. This charge directly strengthens the polarization of the carbon hydrogen bond in the methyl group.

2. The effect of nitro, phenyl, and dinitrophenyl groups conjugated with the imino group of the imidazole ring can only be considered indirect, and results from the blocking of the unshared pair of electrons of the second nitrogen atom, and in the same way as in the case of the presence of an onium nitrogen, to remove the possibility of decreasing the positive charge of the nitrogen atom. The strongest supplementary activating group in this case is the nitro in position 5 of the benzimidazole ring.

3. The above groups do not have any noticeable effect on the methyl group when introduced into an imidazole ring which lacks an onium nitrogen.

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Received November 20, 1952.

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\* See Consultants Bureau Translation, page 1721.

## CLEAVAGE OF LIGNIN WITH METALLIC SODIUM IN LIQUID AMMONIA

### VI. ACTION OF METALLIC SODIUM IN LIQUID AMMONIA ON FIR WOOD

A. F. Semechkina and N. N. Shorygina

Several years ago, the authors found that lignin isolated from fir wood was cleaved by the action of metallic sodium in liquid ammonia at  $-33^{\circ}$  into low molecular substances among which a considerable part were phenolic derivatives of phenylpropane. It was also shown that natural lignin not isolated from the wood was also cleaved by analogous treatment under the same conditions with the formation of phenolic substances soluble in ether [1-6].

Freudenberg and co-workers [6] treated fir wood flour with metallic potassium in liquid ammonia solution at  $20^{\circ}$ . The wood was cleaved into the following components: cellulose with a yield of 46-48% of the weight of the wood used, which contained nono-cellulose impurities; lignin with a yield of 26-28% of which a part (16-18%) of the weight of the wood, was soluble in methanol, part (3%) was soluble in 1% acetic acid, and part (7-8%) was insoluble in these solvents, but was soluble in dilute alkalies, and 3-pentosans with a yield of 5% of the weight of the wood. According to Freudenberg, the main part of the pentosans was destroyed by metallic sodium in ammonia. Freudenberg isolated no individual lower molecular compounds.

It seemed important to determine whether or not phenols which were isolated from copper ammonium fir lignin, are obtained by the cleavage of natural lignin (unisolated from the wood fibers). An affirmative answer would show the close resemblance between the structures of natural and isolated lignin.

In contrast to Freudenberg, who worked with small amounts of wood (5 g of fir flour), the authors treated 30-50 g of fine fir shavings with metallic sodium solution in one experiment. The reaction was conducted at a temperature below the boiling point of ammonia. As a result, the wood was cleaved into the following components: cellulose with a yield of 34.4%, hemicelluloses, with a yield of 8.3%, and lignin with a yield of 9.2%. In addition, lower molecular products soluble in ether were obtained with a yield of 7.5%, and products of the destruction of carbohydrates and lignin soluble in water, with a yield of 12.3%. 28% of the weight of the wood could not be accounted for. The cellulose was a light, almost white, fibrous material, with the following composition: (in %): C 44.0, H 6.38,  $\text{OCH}_3$  0.99. The hemicelluloses (substances soluble in alkali and insoluble in alcohol), which were a powder-like product, had the composition (in %): C 44.76, H 6.45,  $\text{OCH}_3$  2.03.

The presence of methoxyl groups in the cellulose, as well as in the hemicelluloses, even with a somewhat lower carbon content, is of great interest. It indicates that the presence of methoxyl groups is not caused by impurities of the lignin hydrocarbons, which are completely separated under the reaction conditions used, but are the result of the presence of these groups in the carbohydrates themselves.

An analogous conclusion was made by Freudenberg for beech wood carbohydrates. He obtained substances of carbohydrate character containing a considerable amount of methoxyl groups by the treatment of beech wood with metallic potassium in liquid ammonia. Freudenberg did not mention anything on the formation of methylated carbohydrates from fir wood on treating it with potassium in liquid ammonia.

Dihydroeugenol was isolated from the ether-soluble lower molecular products of the decomposition of the wood, and was identified in the form of the benzoate. Characteristically, a considerably higher amount of lower molecular phenolic substances, based on the amount of lignin in the wood (24.75% of the weight of the lignin determined in the wood by means of the sulfuric acid method) was obtained from the fir wood by a single treatment with metallic sodium in liquid ammonia, than from the isolated lignin (about 8%). The lower molecular substances were obtained with a total yield 28% only after many treatments of the copper ammonium fir lignin with a solution of sodium in liquid ammonia [1].

The yield of the lignin obtained from the fir wood upon treatment with metallic sodium in liquid ammonia was found to be very small and was only 9.2% of the weight of the wood (30.33% of the amount of lignin determined in the wood by the sulfuric acid method). The lignin had the form of a yellowish powder, the following composition

(in%): C 60.55, H 6.58, OCH<sub>3</sub> 5.45. The methoxyl groups content in the lignin must be explained by the fact that part of them contained in the lignin were cleaved under the conditions of the reaction. If the amount of lower molecular acidic products, which were soluble in ether formed during the cleavage with metallic sodium, and which were, evidently, obtained from the lignin, was added to the amount of lignin isolated from the reaction mixture, then the total yield of the lignin would be  $9.2 + 7.5 = 16.7\%$ .

Part of the products of the destruction of the lignin can be found in the water soluble decomposition products, since these products are always formed to an extent of about 20% of the isolated lignin during the treatment with a solution of sodium in liquid ammonia. If these results are conditionally applied for natural lignin, too, then the amount of lignin, together with its destruction products, is again increased by 6.06% (20% of 30.3%), and is, therefore,  $16.7 + 6.06 = 22.76\%$  of the weight of the wood. The yield, based on the "sulfuric acid lignin" contained in the wood, is equal to 75.1%.

It is interesting that Freudenberg and co-workers separated almost all of the lignin contained in the wood by treating wood flour with a solution of metallic potassium in liquid ammonia at 20°. A considerable amount (16-18% of the weight of the wood) contained 15.36% of methoxyl groups, i.e., it was only slightly changed lignin (it was soluble in CH<sub>3</sub>OH).

An intense decomposition of part of the lignin to lower molecular substances occurred in the author's experiments.

The fact of the easy separation of the lignin from the carbohydrates leads to the suggestion that it is bound with the carbohydrate components in the walls of the vegetable skeleton by chemical bonds which are readily cleaved by metallic sodium.

It is known that simple ether bonds are cleaved by metallic sodium under these conditions with a varying degree of facility, which depends on their nature. Aromatic ethers are cleaved very easily, aralkyl less readily, and the aliphatic, not at all [7, 8]. The presence of aromatic ether bonds in the lignin carbohydrate complex is impossible. Aliphatic ether bonds are excluded on the basis of experimental results. Therefore, only the aralkyl ether bond remains. However, on the basis of the known facts, it is difficult to imagine how aralkyl ether bonds could be cleaved quantitatively under the conditions of the experiment.

It is known that glycosides with aliphatic aglucones are not cleaved by sodium, but glycosides with aromatic aglucones are in certain cases. Thus, phenylglucoside was cleaved by metallic potassium in liquid ammonia [6]. Coniferin is partially cleaved by a solution of metallic sodium in liquid ammonia; arbutin, however, is not cleaved at all [8].

It is possible that the carbohydrates are combined with lignin in the vegetable fibers by means of ketal or poly-ketal bonds resulting from the keto groups in the lignin and the hydroxyl groups in the carbohydrates. It is regrettable that up to now there are no data on the stability of ketals from the lignin type keto groups and the hydroxyl groups of carbohydrates to the action of sodium in liquid ammonia. We know, however, that benzophenone dimethyl ketal is almost completely cleaved by a solution of sodium in liquid ammonia at -33° [8].

#### EXPERIMENTAL

A piece of the trunk of a freshly-cut 25-year old fir, cut 1 m from the root and 2 m in length, was cleaned from cork and was converted into thin shavings. An average sample of the shavings was dried in a desiccator over phosphoric anhydride, and analyzed.

Composition of the wood: cellulose, by the chloroform method, 53.4%, pentosans (according to Tollins), 11.2% lignin by the F. P. Komarov modification of the sulfuric acid method, 28.4%.

30 g of the shavings was extracted twice by an alcohol-benzene mixture (1:1) and treated 2 times at room temperature with a 5% solution of sodium hydroxide with shaking in order to remove the hemicellulose part. The shavings were washed with water, 2% acetic acid solution, and again with water, and dried first in the air, and then over phosphorus pentoxide. The yield of the purified shavings was 91.4% of the starting ones. The amount of lignin in the shavings treated in this manner was 30.3% (according to F. P. Komarov's method).

The absolutely dry shavings were poured into a reaction vessel, placed in a large Dewar vessel, and covered with 1000 ml of liquid ammonia; 100% of the weight of the wood of metallic sodium was added to it in several portions. The reaction mass was stirred daily. The reaction was completed in 7 days (decolorization of the ammonia solution). Moist ether was added to the residue after the removal of the ammonia, and the reaction mixture



was left to stand overnight; the ether was then poured off, and water was added to the residue. A considerable amount of the reaction mass dissolved.

Isolation of cellulose. The entire mass was extracted with ether, the water-insoluble residue was filtered from the alkaline solution, washed with dilute alkali solution, then with water, and dried, first in the air, and then over  $P_2O_5$ . 10.32 g cellulose was obtained in the form of an almost white fibrous material. It had the following elementary composition:

4.261, 4.308 mg substance: 6.870, 6.845 mg  $CO_2$ ; 2.430, 2.440 mg  $H_2O$ . Found %: C 44.00, 43.99; H 6.38, 6.27.  $C_6H_{10}O_5$ . Calculated %: C 44.44; H 6.15. 16.56, 15.67 mg substance: 1.6, 1.49 ml 0.02 N  $Na_2S_2O_3$ . Found %:  $OCH_3$  1.0, 0.98.

Isolation of the lower molecular phenolic substances. The aqueous alkali solution remaining after the removal of the cellulose, was extracted with ether. The ether extracts were dried, and the ether was removed. The residue, 0.37 g (1.23% of the weight of the wood), was a transparent, oil-like, light yellow liquid. It was vacuum distilled at 0.1 mm. 0.2 g of an almost colorless oil-like liquid was obtained.

0.2 g of the substance, 1.2 g of benzoyl chloride, and 10 g of a 15% sodium hydroxide solution were shaken, whereby a crystalline mass formed rapidly. The crystals melted at  $74^\circ$  after recrystallization from alcohol. A mixed melting point with dihydroeugenol benzoate gave no depression.

The aqueous alkali solution after extraction with ether, was acidified to Congo with 10% sulfuric acid. A voluminous precipitate of lignin and hemicelluloses formed. The mixture (acidic solution and precipitate) was extracted many times with ether. The ether extracts were dried, and the ether was removed.

1.88 g of a thick dark liquid (6.27% of the starting wood) was obtained. The liquid was distilled at 0.1 mm. Two fractions were obtained, and a considerable amount of the substance tarred.

Fraction 1 boiled below  $100^\circ$  at 0.1 mm and was a clear mobile oil; 0.45 g.

3.360 mg substance: 8.825 mg  $CO_2$ ; 2.634 mg  $H_2O$ . Found %: C 71.66; H 8.77.  $C_{15}H_{14}O_2$  (dihydroeugenol). Calculated %: C 72.28; H 8.43.

The substance formed a crystalline benzoate melting at  $68-71^\circ$  upon shaking with benzoyl chloride and alkali.

5.130 mg substance: 14.284 mg  $CO_2$ ; 2.559 mg  $H_2O$ . Found %: C 75.67; H 6.44.  $C_{17}H_{16}O_2$ . Calculated %: C 75.53; H 6.71.

The benzoate obtained melted at  $68-71^\circ$  when mixed with dihydroeugenol benzoate. A mixed sample with eugenol benzoate (m.p.  $68-70^\circ$ ) gave a depression and melted at  $57-60^\circ$ . Therefore fraction 1 obtained by the distillation of the ether extracts of the acidified reaction mixture was also dihydroeugenol.

Fraction 2, a thick, syrupy liquid boiled above  $100^\circ$  at 0.1 mm; it was not identified.

Isolation of lignin. The precipitate which formed on the acidification of the alkaline solution with 10% sulfuric acid, was filtered, after the extraction of the entire mass with ether, on a glass filter, and then treated many times with hot alcohol. The combined alcoholic extracts were dried with anhydrous sodium sulfate, and the alcohol was distilled in vacuum to a small volume. The liquid was poured into a small dish and left in a vacuum desiccator over sulfuric acid. Several days later, the dry residue was transferred into a desiccator containing phosphorus pentoxide.

The yellowish powdered dry lignin weighed 2.76 g (9.2% of the weight of the wood taken).

4.027, 4.405 mg substance: 8.931, 9.780 mg  $CO_2$ ; 2.378, 2.630 mg  $H_2O$ . 19.04 mg substance: 17.36 ml 0.02 N  $Na_2S_2O_3$ . Found %: C 60.52, 60.58; H 6.66, 6.51;  $OCH_3$  9.43.

2 g of the lignin obtained was covered with 100 ml of liquid ammonia; part of the lignin dissolved, the other part became plastic and was converted into a soft state. 2 g of metallic sodium was added to the mixture, and the reaction and the processing were conducted in the usual manner. The low molecular products were not investigated because there was very little of them, and the undecomposed lignin was analyzed.

3.538, mg substance: 8.395 mg  $CO_2$ ; 2.070 mg  $H_2O$ ; 4.94 ml 0.02 N  $Na_2S_2O_3$ . Found %: C 64.75; H 6.55;  $OCH_3$  9.08.

Isolation of the hemicelluloses. After the removal of the lignin, the alcohol-insoluble residue was dried, first in the air, and then over  $P_2O_5$ . The hemicelluloses obtained were in the form of a grayish powder.

7.070, 6.915 mg substance: 11.545, 11.370 mg  $CO_2$ ; 4.065, 4.006 mg  $H_2O$ . 4.84 mg substance:  
0.93 ml 0.2 N  $Na_2S_2O_3$ . Found %: C 44.56, 44.87; H 6.43, 6.47;  $OCH_3$  1.97.  $C_6H_{12}O_6$ .  
Calculated %: C 44.44; H 6.15.  $C_5H_8O_4$ . Calculated %: C 45.46; H 7.04.

#### SUMMARY

1. Fir wood was readily cleaved into its components by treatment with a solution of metallic sodium liquid ammonia at  $-33^\circ$ .
2. The isolated polysaccharides, cellulose and hemicelluloses contained a small amount of methoxyl groups which indicated that not all of the methoxyl groups in the fir wood were contained in the lignin; part of them belonged to the carbohydrate.
3. The lignin was decomposed to a great extent by the action of metallic sodium in liquid ammonia on the wood. 7.5% of the weight of the wood or 24.6% of the lignin, determined by the sulfuric acid method, was converted into lower molecular substances soluble in ether, and partly vacuum distillable.
4. Dihydroeugenol, previously obtained from isolated lignin by treating it with metallic sodium in liquid ammonia, was isolated from the destruction products of the lignin. This indicated the close relationship between isolated and natural lignin.

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Received May 15, 1953

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